FINAL REPORT

WORKSHOP ON HYDROGEN STORAGE AND GENERATION FOR MEDIUM-POWER AND -ENERGY APPLICATIONS

8-10 April 1997
Orlando, Florida

Sponsors:
U.S. Army Research Office
Office of Research and Development, CIA

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SOUTH CAROLINA

Department of Chemical Engineering

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13. This report summarizes the Workshop on Hydrogen Storage and Generation Technologies for Medium–Power and –Energy Applications which was held on April 8-10, 1997 at the Radisson Hotel Orlando Airport in Orlando, Florida. There were 70 participants, representing private industry, national laboratories, the Department of Defense, and academia. The Workshop was sponsored by the U.S. Army Research Office and by the Office of Research and Development of the Central Intelligence Agency. The objective of this workshop was to review and summarize what is known or under development concerning hydrogen storage and generation technologies that are potentially applicable for use in small- to medium-sized PEM fuel cell systems. The Workshop participants were instructed to consider three specific fuel cell power systems: a 300 watt (W) fuel cell with 10 kWh energy storage, a 100 W person-portable fuel cell with a minimum of 1 kWh energy storage, and a 10 W fuel cell with 90 kWh energy storage. These three power systems were suggested by the Workshop sponsors because of anticipated future military and defense applications. In addition, power supplies of this size may also have significant applications in the commercial sector.

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1. EXECUTIVE SUMMARY

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This report summarizes the Workshop on Hydrogen Storage and Generation Technologies for Medium–Power and –Energy Applications which was held on April 8-10, 1997 at the Radisson Hotel Orlando Airport in Orlando, Florida. There were 70 participants, representing private industry, national laboratories, the Department of Defense, and academia. The Workshop was sponsored by the U.S. Army Research Office and by the Office of Research and Development of the Central Intelligence Agency. The objective of this workshop was to review and summarize what is known or under development concerning hydrogen storage and generation technologies that are potentially applicable for use in small- to medium-sized PEM fuel cell systems. The Workshop participants were instructed to consider three specific fuel cell power systems: a 300 watt (W) fuel cell with 10 kWh energy storage, a 100 W person-portable fuel cell with a minimum of 1 kWh energy storage, and a 10 W fuel cell with 90 kWh energy storage. These three power systems were suggested by the Workshop sponsors because of anticipated future military and defense applications. In addition, power supplies of this size may also have significant applications in the commercial sector.

The charge to the Workshop participants as well as the Workshop agenda are given in Section 2 of these proceedings. The Workshop began with a Plenary Session which occupied Day 1 and a portion of Day 2. A total of eighteen experts were invited to speak in the Plenary session. Seven speakers from DoD, CIA, and DOE reviewed both the present research and development status of hydrogen storage and generation systems, as well as the anticipated needs of the defense sector. The remaining eleven invited speakers provided a technological and scientific overview of selected hydrogen storage and generation materials and systems. Section 3 of these proceedings contains a review of the plenary session and copies of all the viewgraphs presented in the plenary session.

At the conclusion of the invited presentations, workshop participants were assigned to one of three working groups for detailed technical discussions and preparation of summary reports. The working group on Physical and Absorptive Storage (Group 1) addressed technologies such as compressed hydrogen gas storage, reversible absorptive storage using metal hydrides, and reversible absorptive storage using carbonaceous materials. The working group on Chemical Hydrides and Related Materials (Group 2) addressed technologies including irreversible hydrolysis of classical chemical hydrides, irreversible solid state decomposition of chemical hydrides, reversible hydrogenation/dehydrogenation of hydrocarbon shuttle compounds, and organosilanes and organoboranes. The working group on Thermal and Catalyzed Processes (Group 3) considered technologies such as partial oxidation of hydrocarbons and alcohols, thermal decomposition of ammonia, and catalytic decomposition of hydrocarbons. The feasibility of using "mesoscopic processors" (chemical process equipment on the order of cm in dimension) to produce hydrogen was discussed in Group 3.

Participants in each working group were encouraged to make additional presentations of technical materials. The working groups were charged with developing estimates of weight and volume required to fabricate a hydrogen generation system for the three fuel cell systems described above. The working groups were also charged with discussing and summarizing additional issues such as safety, likelihood of success, time to implementation, and resources required for development of hydrogen generation devices based on the different technologies. Section 4

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of these proceedings contains an overview of each working group prepared by the authors of this report. Section 4 also contains the written summaries prepared by the working groups, as well as additional viewgraphs presented to the working groups.

During the last half-day of the Workshop, the participants re-convened to hear and discuss the results and recommendations developed by the three working groups. The findings of the three working groups are summarized below.

Availability of Technologies for Field-Testing

The stage of development of the various technologies is given below. Findings are grouped according to the participants' views on whether a given hydrogen storage/generation technology is or should be available for field-testing in the short-term (0-3 years), medium-term (3-5 years), or long-term (5+ years). The technical barriers and resources needed to bring the technologies to maturity are discussed later in this report.

Technologies available for field-testing in 0-3 years
- Hydrogen storage in lightweight, pressurized tanks
- Reversible, low-temperature, low capacity metal hydrides
- Reversible, high-temperature, high capacity metal hydrides
- Hydrolysis of classical chemical hydrides
- Solid state reaction of classical chemical hydrides
- Thermal decomposition of ammonia

Technologies available for field testing in 3-5 years
- Pressurized storage in glass microspheres
- Hydrolysis of novel silanes and boranes
- Reversible hydrogenation/dehydrogenation of cycloalkanes using known heterogeneous catalysts
- Absorptive storage on fullerenes

Technologies available for field testing in > 5 years
- Partial oxidation (POx), steam reforming, or combined oxidation/reforming (PrOx) of hydrocarbon or alcohol fuels in mesoscopic processors
- Single wall carbon nanotubes
- Graphite nanofibers
- Reversible hydrogenation/dehydrogenation of cycloalkanes using novel homogeneous catalysts
- Hydrolysis or thermal reaction of ligand-stabilized chemical hydrides

Summary of Material Characteristics

Technologies for storage of hydrogen span a broad range of materials science. Table 1 summarizes the material characteristics of the technologies discussed in this workshop. The first column reports the hydrogen storage yield as kg of hydrogen theoretically available per kg of materials. "Materials" is defined here as the stored hydrogen plus any substrate, co-reactant (*e.g.*, water), or other substance intrinsic to the storage technology. In the particular case of

compressed hydrogen gas storage, the container itself is intrinsic to the technology and its mass included in the calculation of storage efficiency. For the remaining technologies the weight of containers is not reflected in Table 1. The second, third, and fourth columns are equivalent hydrogen storage capacities in terms of Ah/kg (1 kg H_2 = 26,800 Ah), Wh/kg, and Wh/l. The latter two equivalencies assume that the hydrogen is consumed in a fuel cell stack operating at 0.7 V. Columns 3 and 4 show the effective density of the storage materials. The column entitled "Thermal Burden" shows whether heat has to be added or removed in the hydrogen production step. In the case of pressurized hydrogen, for example, hydrogen is released with zero energy input, but a low temperature metal hydride requires several thousand kilojoules to release all the hydrogen theoretically available. The final column is a partial list of required ancillaries (valves, regulators, reactors, pumps, etc.) which are required to assemble a working system.

Summary of Mission-Specific Weight and Volume Estimates

Workshop participants were asked to estimate the weight and volume of a system (materials plus ancillaries) to meet the three specific example applications described above. Their estimates are given in Table 2. It must be remembered that there is a great deal of uncertainty associated with those estimates for technologies that are medium-term and long-term in anticipated availability. Some of these technologies are in the research stages and no prototypes have been fabricated. For the near-term applications, in most cases, working prototypes have been made and tested, and therefore the weight and volume estimates have a stronger basis. While some of the data contained in this table may have been published elsewhere by individual authors, it is stressed that the compilation of data in Tables 2 and 3 has not been submitted for external peer review.

Critical Research and Development Needs

Participants were asked to identify the additional research and development activities which would be required to bring a given hydrogen storage and generation technology to maturity. Because the technologies are in different stages of development, the term "maturity" has to be defined with flexibility. Some technologies are already in the prototype and field-test stage of development, so "maturity" would mean developing a field-certifiable unit meeting all requirements for operability and safety. For technologies which are still in the research stage, maturity means bringing the technology to a point where a prototype storage and delivery system could be built. Certain research and development needs were identified in the working groups as significantly affecting most or all of the hydrogen storage and generation technologies discussed. These are:

- Miniaturization (that is, volume and weight) of components and ancillaries (*e.g.*, pumps, blowers, regulators, heat exchangers, reactors, separators)
- Starting, stopping, and controlling hydrogen delivery (*e.g.*, fundamental understanding of reaction kinetics, improved sensors, control algorithms, control systems)
- Hydrogen purity and removal of contaminants
- Scaling laws (technologies may work for larger power/energy requirements but uncertainty increases for smaller requirements)

- Temperature-related issues (*e.g.,* thermal signature, heat sources or sinks for endo- or exothermic reactions, temperature limits of fuel cell membranes, coupled endo- and exothermic reactions during startup)
- Water management (if required) for the hydrogen source and integration with fuel cell water management
- Toxicity, recycling, treatment, or disposal of materials and any by-products (especially important for novel materials being developed)

Finally, the issue of safety was discussed extensively in the working groups and in the plenary and wrap-up sessions. Whether engaged in basic research or applied systems development, participants expressed uncertainty about how to assess safety during the design of hydrogen storage and production systems. Even though some technologies may require significant additional R&D before field-testing, the basic concepts of system design can usually be outlined at a fairly early stage of development, and the broad safety issues can be anticipated. Therefore, the DoD should consider consulting with operations personnel to develop safety guidelines that will provide clear bounds for the development of hydrogen storage and delivery systems.

Table 1. Summary of Material Characteristics

Technology	Theoretical H$_2$ yield (kg H$_2$/ kg materials)	Ah/kg materials	Wh/kg materials (at 0.7 V)	Wh/L materials (at 0.7 V)	Thermal Burden (J/kg materials)	Required Ancillaries
Working Group 1: Physical and Absorptive Storage						
Pressurized tanks	< ~ 0.18	< ~ 4820	< ~ 3380	435 (5 kpsi) 732 (10 kpsi) 958 (15 kpsi)	0	Burst disc, regulator
Glass Bubbles	0.094 @ 6000 psi (unsupported)	2520	1760	320	0	Release device, *e.g.,* mechanism to crush spheres
Low temp. metal hydride	0.0175	470	330	1800	+16,800	Heat/cool, low pressure container
High temp. metal hydride	0.060	1610	1130	1630	+35,000	Heat source, exchanger (320°C)
Mg- 23 at% Ni	0.054	1445	1011	1630	+32,000	"Thermite Heater"
NaAlH$_4$	0.060	1700	1300	1480	-55,000	Wafer reaction catalyst
AlH$_3$	0.10	2400	1900	2000	-10,000	Regulator, reactor, binder, igniter
Fullerene	0.07	1680	1300	2000	+41,000	Heater (400°C)
Single wall nanotubes	0.02 - 0.05	540 - 1340	380 - 940	560 - 1010	~ 0	Bleed valve, lt. wt. tank
Graphite nanofibers	0.20 - 0.50	5360-13400	3752-9380	1900-4700 @ 0.5g /cm^3	~ 0 for 90% release	Lt. wt. tank
Working Group 2: Chemical Hydrides and Related Materials						
Silanes-Boranes (hydrolysis)	0.10 ± 0.02	2600 ± 400	1900 ± 300	1650 ± 250	Unknown, but slightly exothermic	Metering pump, container, solvent (H$_2$O)
Solid state chemical hydrides	0.08 - 0.1	2680	1876	1876	+33,000	Holding tank (2000 psi) cartridge, temp. management
Cycloalkanes (dehydrogenation)	0.073	1950	1361	1211	Heat input required, must heat to 150-250° C	Valves, H$_2$ gas perm. membrane, temp. management
Classical hydrides (hydrolysis)	0.073	1950	1369	460	+86,820	Valves, room for expansion, temp. management

Table 1 (continued). Summary of Material Characteristics

		Working Group 3: Thermal and Catalyzed Processes				
Technology	Theoretical H_2 yield (kg H_2/ kg materials)	Ah/kg materials	Wh/kg materials (at 0.7 V)	Wh/L materials (at 0.7 V)	Thermal Burden	Required Ancillaries
Ammonia: 2 NH_3 = 3 H_2 + N_2 (thermal decomp.)	0.176	4560	3190	2459	High temp., heat req'd	Smell; toxicity; adsorption req'd; widely available
Methanol + ½ O_2 = CO_2 + 2 H_2 (POx)	0.083	2144	1501	1187	Autothermal	Lowest peak temp.; CO clean up req'd.; methanol toxicity
Methanol + H_2O = CO_2 + 3 H_2 (steam reforming)	0.12	3216	2345	2111	High temp., heat req'd	Toxicity; water req'd; CO scrub
Propane + 3 H_2O = 3 CO + 7 H_2 (steam reforming)	0.143	4150	2906	2205	High temp., heat req'd	Low pressure feed; 730 C; Additional CO scrub, shift, or POX ; sulfur
Methane + H_2O = CO + 3 H_2 (steam reforming)	0.176	4824	3377	750	High temp., heat req'd	Higher pressure gas; additional CO scrub, shift, or POX ; sulfur
Butane + 4 H_2O = 4 CO + 9 H_2 (steam reforming)	0.138	3711	2598	1971	High temp., heat req'd	Low press. feed; additional CO scrub, shift, or POX ; sulfur
Octane + 8 H_2O = 8 CO + 17 H_2 (steam reforming)	0.132	3484	2439	2195	High temp., heat req'd	Complex mixture; additional CO scrub, shift, or POX ; sulfur
#2 diesel fuel + H_2O (steam reforming)	0.12	3208	2242	2018	High temp., heat req'd	Highest sulfur; highest operating temp.; additional CO scrub, shift, or POX ; coking

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Table 2. Summary of Mission Specific Estimates

Technology	Est. wt.(kg) 300 W, 10 kWh system	Est. wt. (kg) for 100 W, 1 kWh system	Est. wt. (kg) for 10 W, 90 kWh system	Est. vol. (L) for 300 W, 10 kWh system	Est. vol. (L) for 100 W, 1 kWh system	Est. vol. (L) for 10 W, 90 kWh system
Working Group 1: Physical and Absorptive Storage						
Pressurized tanks (1.5 safety factor @ 300 K)	4.22 (5 kpsi) 4.65 (10kpsi) 5.05 (15kpsi)	1.39 1.44 1.48	27.0 30.8 34.4	24.4 15.3 12.4	2.5 1.5 1.2	219 137 111
Glass bubbles on film roll @ 9000 psi	9.1 (excl. release device)	1.1	80	32	6	272
Low temp. metal hydride	30.5	3.1	270	12	1.12	108
Mg-23%Ni w/thermite and tanks (~same for other high temp. metal)	15	1.5	142	10.7	1.07	96
Fullerene	16.5 (8 kg containment)	1.65	85	7.4 (30% tank vol)	0.74	51
Single wall nanotubes (*See Note Below*)	29-11.7 (12 ang-20 ang & 10% tank wt)	2.9-1.2	257-109	24-13 (7.5% tank with 80% max packing)	2.4-1.4	1215 - 218
Graphite nanofibers	4.1-5.6 (~3 kg tank)	3.1-3.3	12.6-27	2.1-5.2 (0.5 g/cm^3 loading)	0.2-0.5	19-47
NaAlH$_4$ (incl. H$_2$O)	11	1.2	110	13	1.6	75
AlH$_3$ (dry)	11	1.2	100	11	1.1	65
Working Group 2: Chemical Hydrides and Related Materials						
Classical Hydrides (hydrolysis)	7.3	0.73	65	9.5	0.95	85
Silane/Borane (hydrolysis)	5.3 ± 0.8	0.53 ± 0.08	47 ± 8	6 ± 1	0.6 ± 0.1	54 ± 8
Solid-state chemical hydrides	7 kg (reactants), 1 kg (hardware)	0.7	63	7	0.7	63
Cycloalkanes (dehydrogenation)	7.4	0.74	66	8	0.8	74

Note: Theoretical calculations predict decreased hydrogen packing density as nanotube diameter increases.

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Table 2. (continued). Summary of Mission Specific Estimates

Technology	Est. wt.(kg) 300 W, 10 kWh system	Est. wt. (kg) for 100 W, 1 kWh system	Est. wt. (kg) for 10 W, 90 kWh system	Est. vol. (L) for 300 W, 10 kWh system	Est. vol. (L) for 100 W, 1 kWh system	Est. vol. (L) for 10 W, 90 kWh system
Working Group 3: Thermal and Catalyzed Processes						
Mesoscopic hardware/fuel	0.3-0.4/5.5	0.15-0.24/.55	0.08-0.1/49.5	0.1-0.16/7.86	0.05-0.08/0.79	0.025-0.035/70.7
Ammonia hardware/fuel	1.7/4	0.731/0.4	0.16/36	0.9/4.9	0.3/0.5	0.1/45
Hot Spot hardware /fuel	0.5/8.8	0.2/0.88	0.1/79	0.5/10	0.2/1	0.1/90
Mini-hybrid POx based on current hardware (1 yr) system/fuel	1.4/5.5	0.5/0.55	0.06/49.5	1.1/7.86	0.4/0.79	0.06/70.7
Mini-hybrid POX based on next generation hardware (3 yrs) system/fuel	0.6/5.5	0.2/0.55	0.06/49.5	0.5/7.86	0.2/0.55	0.05 /70.7
Steam reforming hardware/fuel	5.6/5.5	2.6/0.55	0.5/49.4	3.5/7.86	1.63/0.79	0.3/70.7

2. WORKSHOP CHARGE AND ORGANIZATION

2. Workshop Charge and Organization

Small and medium-power polymer electrolyte membrane (PEM) fuel cells may find new uses in military systems, space systems, transportation, and in consumer applications. Both portable and stationary power sources are of potential strategic and commercial value. A key limitation to the adoption of PEM fuel cell power sources is the hydrogen source. The objective of the Workshop was to review the current state of development of hydrogen storage and generation for medium-power ($\leq$ 300 W) and medium-energy ($\leq$ 100 kWh) applications. An additional objective was to identify critical research needs and promising opportunities for additional research and development. The emphasis on small- to medium-power and energy applications was chosen by the Workshop sponsors because of military and strategic needs such as person-portable power systems, field-portable battery recharging stations, and long-life, low-power unattended surveillance operations.

The Organizing Committee for the Workshop was chaired by Professor Michael Matthews of the University of South Carolina Department of Chemical Engineering. The other Organizing Committee members were Dr. Ralph White, Chairman of the Department of Chemical Engineering and Director of the Center for Electrochemical Engineering at the University of South Carolina, Dr. Peter Fedkiw of U.S. Army Research Office, and Mr. Joseph Stockel of the Office of Research and Development of the Central Intelligence Agency. The Workshop consisted of a number of invited speakers, joined by additional experts from government, industry, and academia. Through a combination of prepared presentations and organized working groups, a complete survey of the present status of hydrogen storage and generation was obtained. The speakers for the 2-1/2 day workshop are listed in Table 3.

To guide the invited speakers and other workshop participants in focusing their comments, three generic systems were identified: (1) a 300 W fuel cell with 10 kWh energy storage; (2) a 100 W , 1 kWh system with a maximum weight of 3 kg; and (3) a 10 W, 90 kWh system. The 300-W fuel cell is a prototype of a power plant which would serve as a stationary battery charging station for soldiers in the field. Such a power plant would be light enough to be rapidly deployed in the field, and attitude sensitivity would not be an issue. The person-portable fuel cell would power electronic devices for an individual soldier; consequently, both the fuel cell and the hydrogen source must be insensitive to attitude and must withstand the rigors of combat. The third system could serve as a power supply for a remote surveillance installation.

Table 3. Workshop Speakers

Day 1 - Tuesday, April 8

Speaker	Topic
Dick Paur, ARO	Workshop Goals & Objectives
Jim Stephens, CECOM	Overview, Field Applications and Specifications
Deryn Chu, ARL	ARL Fuel Cell R&D Program
Jay Stedman, Consultant	System Considerations
Joe Stockel, ORD	Hydrogen Storage Research
Jim Ohi and George Thomas, DOE	DOE Hydrogen Storage Programs
Roger Pyon	DARPA Hydrogen Storage Programs
Brian James, Directed Technologies, Inc.	Pressurized Hydrogen Storage
Michael Monsler, W. J. Schafer Assoc.	Energy Film
Ottmar Dengel, Royal Systems	Chemical Hydrides: Solid State H_2 Generation
Subash Narang, SRI	Novel Organosilanes for Hydrogen Storage
Xiaou Liu, MER	Hydrogen Storage Using Decalin
Dave Bloomfield, Analytic Power	Thermal Decomposition of Ammonia
Bob Wegeng, PNL	Compact Fuel Processors/ Microsystem Technologies
Jonathon Frost, Johnson Matthey (UK)	Partial Oxidation of Hydrocarbons
Brian Barnett, A. D. Little	Small Scale Flexible Fuel Processors

Day 2 - Wednesday, April 9

Speaker	Topic
Jim Reilly, Brookhaven National Lab	Metal Hydrides as Hydrogen Storage Media
John Van Zee, USC	Fullerenes for Hydrogen Storage
Nelly Rodriguez, Northeastern University	Graphite Nanofibers for Hydrogen Storage
Break-Out Sessions	Session 1: Absorptive and Physical Storage
	Session 2: Chemical Hydrides and Related Materials
	Session 3: Catalyzed and Thermal Processes

Day 3 - Thursday, April 10

Speaker	Topic
Workshop Wrap-Up	
Mark Debe, Michael Heben	Session 1: Report
Oliver Murphy, Omourtag Velev	Session 2: Report
Frank Rose, Dave Bloomfield	Session 3: Report

3. SUMMARY OF PLENARY SESSION

3. Summary of Plenary Session

Dr. Richard Paur of the U.S. Army Research Office (ARO), co-sponsor of the Workshop, reviewed the workshop goals and objectives. The U.S. Army and other military branches have numerous applications for small power sources on the order of less than one kilowatt-hour (kWh) energy storage. Presently the DoD uses batteries for many small-power applications, but the cost of these and the problems of disposal are significant. The ARO has invested heavily in development of small proton exchange membrane (PEM) fuel cells, and has observed considerable improvements in minimizing the weight and volume of the fuel cell stack. Several prototypes have been built and field demonstrations have been conducted. It is the judgment of many that developing compact, lightweight systems for hydrogen storage and generation is the limiting factor in advancing the implementation of PEM fuel cell power sources. The objectives of the Workshop were to bring together a select group of experts in chemistry, materials science, and engineering from government, industry, and academia to discuss the current state-of-the-art in hydrogen storage and generation. Workshop participants were directed to focus their discussions around three representative small- to medium-sized power sources: 300 watt (W) fuel cell with 10 kWh energy storage, a 100 W person-portable fuel cell with a minimum of 1 kWh energy storage, and a 10 W fuel cell with 90 kWh energy storage. The technical issues associated with developing hydrogen sources to meet these needs were to be discussed, and quantitative estimates of the size and weight of devices were to be estimated as accurately as possible. The goals were to generate new ideas, identify the most promising technologies, and to create synergism so that new systems for storage and generation of hydrogen might be developed.

James Stephens of the U.S. Army Communications and Electronics Command (CECOM) reviewed the field applications and specifications for small fuel cell systems. (Person) portable power systems were defined as producing less than 500 W power, while mobile power falls in the range of 500 W to 1.1 MW. Batteries are presently viewed as too heavy and costly and new sources of battlefield energy are strongly desired. It is anticipated that the first field use will be for niche applications, and that general PEM fuel cell use will follow with further development. PEM fuel cells must be competitive with batteries in terms of weight, cost, and safety. Fuel cell developers should consider systems which augment battery power, and should not focus just on replacement because it is not likely that batteries will be completely replaced. Stephens presented a number of operational requirements which individual soldier power systems must satisfy, such as low weight, durability, reliability, and a user-friendly interface. It is anticipated that the average power demand will be 5 W, with peak power of 20 W, which should be available for missions of up to 7 days (20 hours on, 4 hours off). Another application discussed by Stephens is for unmanned aerial vehicles. Electric power is required for propulsion (< 15 kW) as well as for payload operations (50-200 W). In addition, there are needs for power sources for special operations (set and forget missions), sensor suites with long mission durations, small unit operations, and soldier power. It is critical that equipment developers understand that hydrogen supply logistics must match mission requirements; the mission requirements will not be altered to fit the logistics and performance of the power source.

Deryn Chu of the U.S. Army Research Laboratory discussed fuel cell research at ARL. A major driving force is cost; another is simplifying operations. The Army spent $77.2 million on over 300 different types of batteries in 1996. The Army has been given a directive by Army Chief of Staff General Dennis J. Remer to reduce this cost by 50%. Research at ARL falls under either the 6.1 or 6.2 programs. Presently most of the research is on materials development for

hydrogen fuel cell stack in the 50-150 W power range. The focus has been on improving the electrode/electrolyte interface. Under the D-650 program, ARL is evaluating stack/system performance of a 25 W air-breathing stack and a 100 W stack. They have an SBIR on developing a 50-150 W stack. ARL is also conducting research on materials for direct methanol fuel cells with Johns Hopkins University, examining the effects of surface preparation and different platinum and ruthenium catalysts.

Joe Stockel of the Office of Research and Development, CIA, described his recent projects in hydrogen storage and generation. The missions of interest often concern remote and unattended operation, with long periods of low power consumption followed by large spikes. Among the projects supported were studies of the synthesis of fullerenes and catalytic routes for hydrogen loading (MER Corporation), and development of novel liquid organosilanes which hydrolyze in water (SRI).

George Thomas of Sandia National Laboratory described the broad range of hydrogen storage research which DOE is conducting, which is mostly aimed at larger-scale transportation and utility applications. Reversible metal hydrides and compressed hydrogen are two of the technologies of interest to DOE.

Roger Pyon (DARPA) has supported the development of small hydrogen generators based on the irreversible reaction of chemical hydrides (CaH_2, LiH) with water. AF Sammer has developed units which produce 50 or 100 liters of hydrogen gas. The 100-liter hydrogen system weighs 1 kg and has a volume of 0.92 liters. DARPA has also supported Energy Conversion Devices (ECD) in the development of Mg-based reversible alloy metal hydride storage materials which have a capacity of 5-6 weight percent hydrogen. Hydration occurs at 100 °C and dehydration at 250 °C.

Following the presentations by DoD, DOE, and CIA personnel, Mr. Jay Stedman gave a presentation on the systems aspects of hydrogen fuel cells. Materials scientists, research engineers, and component developers must be aware of the issues involved in coupling a hydrogen source to a fuel cell stack. Furthermore, all parties must be aware of the particular needs and constraints of the user, particularly of the electronic warrior. Among the technical challenges described were: integration of water management between the fuel cell and the hydrogen source (if the source uses or produces water); heat rejection or adsorption; vaporization and condensation of water in transfer lines and components; transient power requirements, response time and start/stop capability; temperature limits on materials and components; thermal signature; shock and vibration resistance; contaminants in "battlefield air"; and orientation sensitivity. It was noted that very small fuel cells are competing with lithium ion batteries, so use of a "special" fuel for the hydrogen source is not necessarily ruled out.

Brian James of Directed Technologies gave the first of several presentations focused around specific technologies. Directed Technologies has been evaluating light-weight, high-pressure composite tanks for storage of compressed hydrogen. These tanks are lined with a thin, metallized polymer liner. The shell is of composite material and the endcaps of high density polyethylene, for example. Pressures of 5,000 to 15,000 psi have been realized. The required safety factor (burst pressure/operating pressure) must be established by the users. Depending on the pressure and size of the storage required, hydrogen storage efficiencies of four to sixteen weight percent have been realized. Efficiency decreases rapidly with the container size because

the weight of ancillaries such as regulators and valves does not decrease proportionally with volume of the tank.

Michael Monsler of W.J. Schaeffer Associates described the use of glass microspheres for hydrogen storage. This approach uses hollow spheres in the 25-200 micron diameter range which are permeable to H_2 at high temperatures but are impermeable at ambient temperatures. Spheres are filled by heating to 250 °C under a high pressure hydrogen atmosphere. Cooling entraps the hydrogen. Pressures of up to 9,000 psi are envisioned. W.J. Schaeffer is exploring means to release the hydrogen by crushing the microspheres mechanically. One of the potential advantages of this approach is safety; the microspheres themselves can be transported in bulk containers which are not pressure vessels.

Ottmar Dengel of Royal Systems presented an extensive list of solid-state mixtures (*e.g.*, NH_4Cl + $LiAlH_4$) which release hydrogen gas upon thermal ignition. The reaction is quite exothermic, many compounds and mixtures are unstable, and therefore only a few formulations are commercially feasible for producing hydrogen generators. A prototype based on NH_4Cl + $LiAlH_4$ has a theoretical yield of 8.4 weight percent hydrogen (excluding ancillaries).

Subash Narang of SRI described a chemistry for generating hydrogen based upon liquid-phase organoboranes. Development and testing of these compounds has been supported by the Office of Research and Development of the CIA. Much of their work has concentrated on synthesis of the compounds, but preliminary reactions with water (sometimes modified with caustic, alcohols, surfactants) have produced hydrogen in yields in excess of 98%. It appears that the reaction rate can be controlled by addition of different substances to water. Hydrogen storage capacities of 4-9% by weight are possible, depending on the specific organosilane chosen. These compounds are liquids at ambient temperatures and therefore systems using small liquid metering pumps to start, stop, and control the reaction appear feasible.

Xiao Liu of MER Corporation described research on storing hydrogen via the catalytic hydrogenation and dehydrogenation of cyclic hydrocarbons. Two-ring hydrocarbons such as decalin are preferred to single-ring and three-ring compounds. Under low pressure, with the aid of a heterogeneous catalyst, hydrogen is released at temperatures in excess of 200 °C. Residual hydrocarbons were separated from hydrogen in the gas phase with the aid of a membrane separator. The best catalyst identified for this reaction is a supported platinum. This process is reversible, and in principle the hydrocarbon shuttle molecule can be used indefinitely. The reaction is endothermic, and therefore some parasitic hydrogen would be consumed to maintain the required reaction temperature.

David Bloomfield of Analytic Power reviewed a number of materials and hydrogen storage technologies, including pressurized gas, solid state reactions, alcohol and hydrocarbon reforming, and the thermal decomposition of ammonia. The cost per kWh of these technologies was presented, along with data comparing fuel cells to the BA5590 battery. Analytic Power is presently developing a thermal ammonia reformer for prototype testing by the U.S. Navy.

Robert Wegeng of Pacific Northwest Laboratories discussed an advanced concept for portable power generation based on compact (cm-size scale) fuel processors, termed "mesoscale processors." This represents a potential paradigm shift in that the weight of the components (reactors, pumps, heat exchangers) would become small compared to the weight of the fuel. Pacific Northwest Laboratories is engaged in a microtechnology program to develop unit operations on

small scales. They have begun work on partial oxidation reactions, with plans to study JP-8 and diesel fuels.

SPEAKERS' PRESENTATION MATERIALS

OVERVIEW, FIELD APPLICATIONS, AND SPECIFICATIONS FOR 5 - 500 WATT FUEL CELL SYSTEMS

PRESENTED TO WORKSHOP ON HYDROGEN STORAGE AND GENERATION FOR MEDIUM-POWER AND -ENERGY APPLICATIONS

APRIL 8, 1997

JAMES STEPHENS, US ARMY CECOM

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THE POWER SPECTRUM

PORTABLE	GRAY AREA	MOBILE POWER
< 500 WATTS		> 500 WATTS TO 1.1 MW

- BATTERY DOMAIN
  - -- TOO HEAVY
  - -- TOO COSTLY
- EXPLORING ALTERNATE TECHNOLOGY
  - -- NICHES FIRST
  - -- GENERAL USE LATER
- HYDROGEN SUPPLY KEY TO FUEL CELL SUCCESS
- MUST COMPETE WELL WITH OR AUGMENT BATT.

- DIESEL / TURBINE POWERED GENERATORS
- COMPETITORS MUST USE DIESEL FUEL

"Power Revolution a Necessity"

"New Sources of Battlefield Energy Would Have Revolutionary Consequences"

Source: ARMY AFTER NEXT "EMERGING STRATEGY"
DEPUTY CHIEF OF STAFF FOR DOCTRINE, TRADOC

REQUIREMENTS: SYNOPSIS

- FEATURES CRITICAL TO SO SOLDIERS: SMALL, LIGHT, CHARGE INDICATOR AND RECHARGEABLE

- INCREASE POWER DENSITY/MAINTAIN COST

- EQUIPMENT LIMITATIONS CAN NOT DICTATE MISSION PLANNING/ ACCOMPLISHMENT

- LIGHTWEIGHT POWER IS AN ALL-OPERATIONS PROBLEM: WAR, OOTW/PEACEKEEPING, AND TRAINING

- POWER SOURCES REQUIREMENTS ARE NOT SOF-UNIQUE, THUS LEVERAGING NEEDED

- LIGHTWEIGHT POWER IS 3RD HIGHEST TECHNOLOGY PRIORITY OF CINCSOC
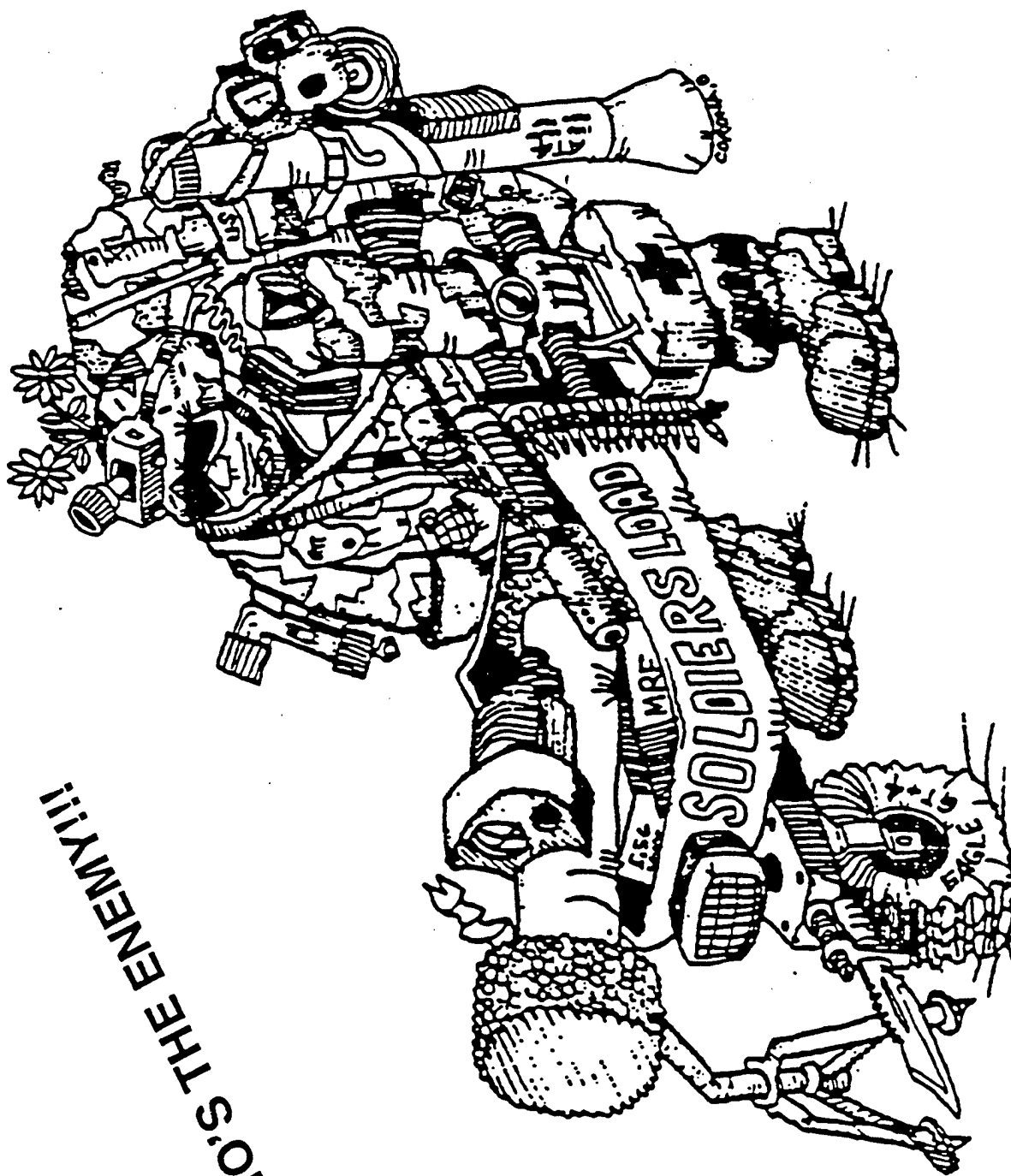
ADVANCED CONCEPTS AND ENGINEERING DIVISION

WHO'S THE ENEMY!!

Individual Warfighter System Size, Weight, and Power

- Soldier Mounted
- < 1 kg
- < 5 watts
- No keyboard
- Very user friendly interface
- Single battery
- Minimal wires
- Plug and play for different applications
- Physically robust

SMALL UNIT OPERATIONS - POWER REQUIREMENT SUMMARY

- AVERAGE POWER DEMAND - 5 WATTS
- PEAK POWER DEMAND - 20 WATTS
- MISSION LENGTH - 7 DAYS
- MISSION DAY PROFILE
  - 20 HOURS ON
  - 4 HOURS OFF
- TOTAL ENERGY DEMAND - 700 WHRS

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Soldier Power System Requirements

- *Small, light weight,* soldier portable
- Continuous power for extended periods
- Necessary power for standard and future equipment
- *Undetectable:* silent, odorless, easily concealed
- *Safe:* stable materials, less hazardous
- Easily supported, maintained
- Durable, rugged, NBC *survivable*
- Modular, interconnective capability
- Operate under all conditions: ECM, smoke, aerosols, fog, rain, haze, dust, wind, snow, icing, NBC, heat, cold, etc......
- Compatible with full protective posture
- Decontaminable w/o efficiency loss

(Source: MNS for Soldier Power System)

Dismounted Battlespace Battle Lab

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- MISSION CANNOT BE CONSTRAINED BECAUSE OF POWER LIMITATIONS (PERFORMANCE)
- SOLDIER MOBILITY MUST NOT BE HAMPERED (WEIGHT)
- UNITS MUST BE ABLE TO TRAIN AS THEY FIGHT (COST)
- SOLDIERS MUST HAVE SAFE POWER (SAFETY)

POWER...
WHEN WE NEED IT...
WHERE WE NEED IT!!

WHERE TOMORROW'S VICTORIES BEGIN

22

UNMANNED AERIAL VEHICLES
POWER REQUIREMENTS SUMMARY

- **POWER REQUIRED <15 Kw (EST)**

- **FUEL CELL ENERGY DENSITY >400 WHRS/KG**

- **MISSION LENGTH/LOITER - DAYS / YEARS @ 20 TO 30 km.**

- **FUEL CELL / SOLAR PANEL / ELECTROLYZER / BATTERY**
  HYBRIDS ENVISIONED

- **POWER REQUIRED FOR:**

  - PROPULSION <15KW

  - SOLAR POWERED ELECTROLYZER ?

  - PAYLOAD 50 - 200 WATTS

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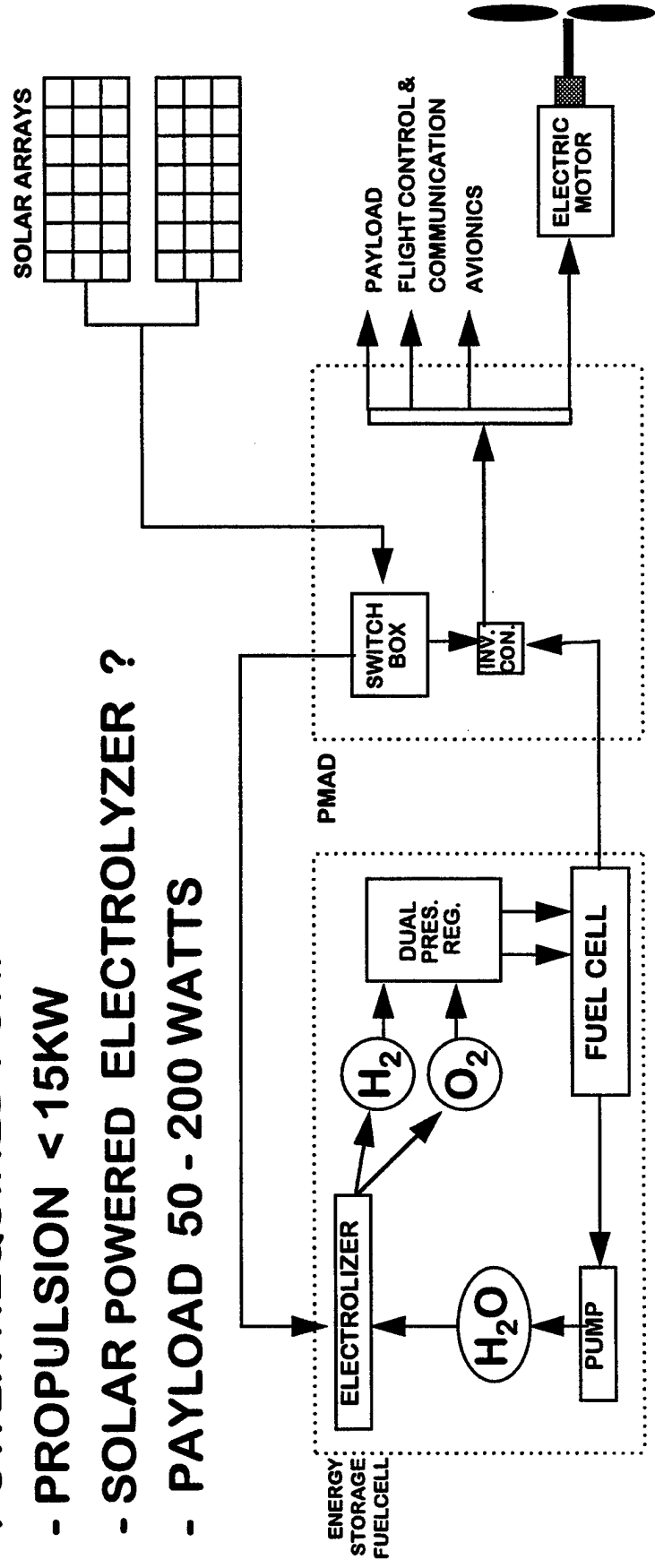
SUMMARY OF POTENTIAL APPLICATIONS FOR MEDIUM-POWER AND -ENERGY FUEL CELLS

APPLICATION	POWER (W)	ENERGY (WHRS)	COMMENT
SPECIAL OPS	50	2500 - 30,000	SOME SET/FORGET MISSIONS.
SMALL UNIT OPERATIONS	5 / 20 P	800	LIGHTWEIGHT
SENSOR SUITES	5 / 50 / 100	240 - 30,000	LONG MISSIONS
SOLDIER POWER	50 / 150	1200 - 2500	MUST COMPETE WITH / AUGMENT BATTERIES
UAV	< 15 (EST)	> 400 WHRS/KG	ROBUST HYBRID

24

CONCLUSIONS

- **HYDROGEN SUPPLY LOGISTICS MUST MATCH MISSION REQUIREMENTS**

- **PEM FUEL CELLS WITH PROPER HYDROGEN SOURCE CAN COMPETE NOW IN NICHE APPLICATIONS**

- **FUEL CELLS WILL COMPLIMENT / AUGMENT BATTERIES BUT NOT REPLACE**

The Status of Polymer Electrolyte Membrane Fuel Cells (PEMFCs) Research and Development Program at Army Research Laboratory

Deryn Chu and Sol Gilman
AMSRL-SE-DC
Electrochemistry Branch
Sensor and Electronics Directorate,
Army Research Laboratory,
2800 Powder Mill Road, Adelphi, MD 20783-1197

The U. S. Army requires extremely lightweight power sources for a variety of portable electronic and other applications. The army consumes many thousands of primary batteries each year to provide power for hundreds of person-portable circuits for communications, sensing, target acquisition and night vision. High energy density primary lithium batteries have been developed and successfully used for many of these applications. After discharge, the primary lithium cells require safe disposal which, besides being costly, involves environmental hazards. Because most of those batteries are of the lithium/sulfur dioxide chemistry which contains lithium salts, organic solvents and sulfur dioxide and thereby threatens the environment until subjected to costly pre-treatment.

Polymer electrolyte membrane fuel cell (PEMFC) is most favored as a portable power supply device primarily because of its light weight and high power density. A PEMFC power source is being developed for a wide variety of applications that now use batteries. These applications range from laptop computers to electric vehicles. PEM fuel cells in conjunction with hydrogen storage offer even higher energy density than lithium cells and can, therefore, enable further reduction in size and weight over lithium batteries. The PEM fuel cell system can be used with a replaceable fuel (e. g., hydrogen stored as metal hydride) cartidge for any practical number of operations without any environmental concern. Small fuel cell systems, if successfully developed, can supplant primary batteries by directly providing power or through use as a silent charger for rechargeable batteries. Rechargeable batteries, in such usage, will last for hundreds of charge/discharge cycles and will correspondingly greatly reduce battery disposal problems.

In the Army Research Laboratory, hydrogen and direct methanol PEM fuel cells have been covered under present fuel cells research and development program. Our present emphasis is on applications which require only one to several hundred watts of power and could be carried by one person, thus employing PEMFCs for other ambient-temperature technology. We have focused on both fundamental and practical research with the ultimate goal of developing PEMFCs which will efficient and economical for both military and commercial applications.

With the hydrogen PEM fuel cell area, three thrusts have been approached. These includes (1) polymer electrolyte membrane, (2) membrane-electrode assembly and (3) stack and system development. **(1)Polymer electrolyte membrane:** In order to reduce the cost of the fuel cell for "dual use" applications, a new low cost membrane needs to be developed. New membranes based on the sulfonic acid salt of poly (p-Phenylene-ether sulfone) (PES) and the sulfonic acid salt of poly (ether-ether ketone) (PEEK) have been synthesized and evaluated under fuel cell

experimental conditions [1]. Modified Nafion membranes made from/lower equivalent weight resins have also been synthesized and characterized [2]. The effects of crosslinking Nafion by electron beam irradiation of Nafion in the presence of various monomers have been studied. Many different types of polymer membranes have also been tested as a electrolyte for a single fuel cell experiment. The best performaning membrane is Nafion 112 [3]. **(2) Membrane-electrode assembly:** The membrane electrode assembly (MEA) is a key component for the PEMFC system. The Army Research Laboratory has developed a new technology to prepare MEA and to improve single cell performance [4]. The MEA prepared in this laboratory has operated at low temperature (50 °C) and ambient pressure with low flow rates of fuel and oxidant (20 cc/min) delivering more than 1A/cm^2 at 0.72 V for a single cell [3]. **(3) Stack and system development:** A novel non-bipolar design for ultralight PEM fuel cells has been initiated [5]. This design is based on assembled a single integrated common polymer electrolyte membrane. Individual cells would be series connected, but share a common electrolyte and gas flow fields. The 100 watt PEMFC stack was successfully tested under different experimental conditions. The stack, without fuel purging, can deliver about 100 watts power output (5 Amps at 20 V) for a short period time (~5 hours). The performance then diminished rapidly. This rapid decrease in performance is probably due to impurity problems. However, other possible reasons such as water management and fuel "cross-over" were not ruled out. The stack, with fuel purging, can deliver 100 watts power output for a longer time. It is apparent that the hydrogen purging parameter is a critical issue for the PEM fuel cell system for power output [6-7]. The results of our study will advance the development of hydrogen fueled PEMFC stack systems.

The only practical fuel at the present time is hydrogen. Using hydrogen for fuel presents severe storage and transportation problems which would be minimized through the use of a liquid fuel such as methanol. Methanol has attracted interest as a fuel because it is inexpensive, widely available, and easily stored and transported liquid. The direct utilization of methanol in fuel cells is a very promising route to the achievement of lightweight high energy density power sources for a variety of applications including power for vehicles, central stations and military communications. Effective catalysis of the electrode processes is a key barrier in all cases. For the first two applications, the problem can be by-passed to some degree by raising the operating temperature or by reforming the fuel. Not so for the communications application which requires low operating temperatures and ultimate in system simplicity.

With present the state-of-the-art fuel cell electrocatalysts, approximately one-third of the available energy is lost at the anode and an equal loss occurs at the cathode. The latter occurs when methanol dissolves in the electrolyte and diffuse to the cathode. This, in turn, may cause a so-called "chemical short" (simultaneous methanol electro-oxidation and O_2 electroreduction) which could have a significant effect on fuel cell power density and fuel efficiency. In order for the direct methanol PEMFC to become a practical energy-production device, the serious problem of anode irreversibility and methanol "cross-over" to poison cathode electrode must be solved. In the Army Research Laboratory, we have addressing both problems in our fuel cells research and development program.

In the area of anodic electrocatalysis, we have developed a procedure for fabricating well-characterized high surface area Pt/Ru catalysts and has shown which phase of such polycrystalline

preparations is most effective in the electrode process [8]. The bifunctional mechanism has been proposed to explain the enhancement of methanol electro-oxidation on Pt-Ru alloy. Therefore, optimization of the Pt-Ru electrocatalyst composition and morphology is important for the development of a high performance direct methanol fuel cell. The BET surface area of Pt-Ru electrocatalysts increases with increasing Ru content up to ~70 atomic percent and then reaches a plateau value. When a comparison is made on the basis of electrode geometric surface area, a ~50 a/o ruthenium electrocatalyst provides the highest activity for methanol electro-oxidation. The methanol electro-oxidation rate is 0.5 orders with respect to methanol concentration (between 0.1 and 2M) for the Pt-Ru (~50:50) alloy electrocatalyst.

The real surface area of Pt-Ru alloy compositions versus the methanol electro-oxidation activity is unknown. The standard method of estimating the surface area is to determine the charge associated with anodic stripping of adsorbed hydrogen. However, this technique cannot be used on catalysts such as Ru or Pt-Ru alloys, which absorb hydrogen into the metal lattice [8-9]. We have standardized scanning tunneling microscopy (STM) based fractal technique to determine the surface area of polycrystalline Pt. Properties of fractal geometry, and principles of statistics were used for internal calibration. The results were verified using conventional charged density measurement through anodic stripping of adsorbed hydrogen. A near-perfect correlation was found between these two independent techniques. The surface area of Pt-Ru alloy electrocatalysts were also determined using the STM-based fractal technique [10].

The search for more efficient methanol tolerant electrocatalysts for O_2 electro-reduction requires a better understanding of the basic process. We have successfully elucidated the mechanism by which methanol diffusing from the anode interferes with oxygen electro-reduction and raise the overpotential of that process [11]. This study indicates that development of more selective cathode electrocatalysts for a direct methanol fuel cell is very important. The search for more efficient methanol-tolerant electrocatalysts for O_2 reduction has been initiated.

References:
[1] S. P. S. Yen, R. Mamone, M. Binder, D. Chu and S. Gilman, unpublished results.
[2] W. H. Buck, "Advanced Proton Exchange Membrane Development For High Performance Fuel Cells", Final Report to Army Research Laboratory.
[3] D. Chu and S. Gilman, 7th International Electrochemical Proceeding Volume, Nov. 1996.
[4] D. Chu, U. S. Patent Pending.
[5] R. Mammone , M. Binder and S. Gilman, U. S. Patent Pending, (Serial Number 08/320,611 Field 10/6/94).
[6] D. Chu, S. Gilman and L. Javris, Electrochemical Society Meeting, Fall 1997.
[7] D. Chu, unpublished results.
[8] D. Chu and S. Gilman, J. Electrochem. Soc., Vol. **143**, No.5, 1685-1690 (1996).
[9] S. Hadzic-Jordanov, H. Angerstein-Kozlowska, M. Vukovic, and B. E. Conway, J. Phys. Chem., **81**, 2271(1977).
[10].V. Lakshminarayanna, R. Srinivasan, D. Chu and S. Gilman Surface Science, 1997.
[11] D. Chu and S. Gilman, J. Electrochem. Soc., Vol **141**, No. 7, 1994.

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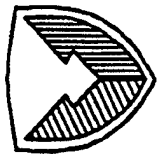
Overview of Army Research Laboratory Fuel Cells Research and Development Program

Deryn Chu and Sol Gilman

Electrochemistry Branch
Direct Energy and Power Sources Division
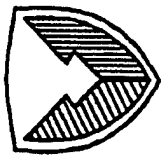**Army Research Laboratory**
Fort Monmouth, NJ 07703-5601

Workshop on Hydrogen Storage and Generation for Medium-Power and Energy Applications

Orlando, FL
April 8-10, 1997

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"Last year the Army spent $77.2 million on 300 different types of batteries, Gen. Dennis J. Reimer (the chief of staff of the Army) has given me a target of reducing battery-related expenditures by 50 percent...."

General Johnnie E. Wilson
Commanding General, AMC
Armed Forces Journal International
August 1996

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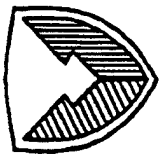
Overview of ARL Fuel Cells Research and Development Program

(I) Hydrogen Fuel Cell

(II) Direct Methanol Fuel Cell

Support and interaction with ARO, CBDCOM, CECOM (TPA) and DARPA

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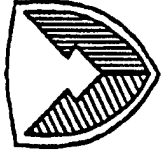
Hydrogen-fueled Fuel Cell Research and Development Program

Objectives: Develop small, simple, lightweight power source with energy density 400 Wh/kg for longer individual soldier applications

Improve state of the art PEM fuel cells technology by providing better materials/components/designs at a lower cost

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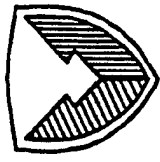
Hydrogen-fueled Fuel Cell Research and Development Program
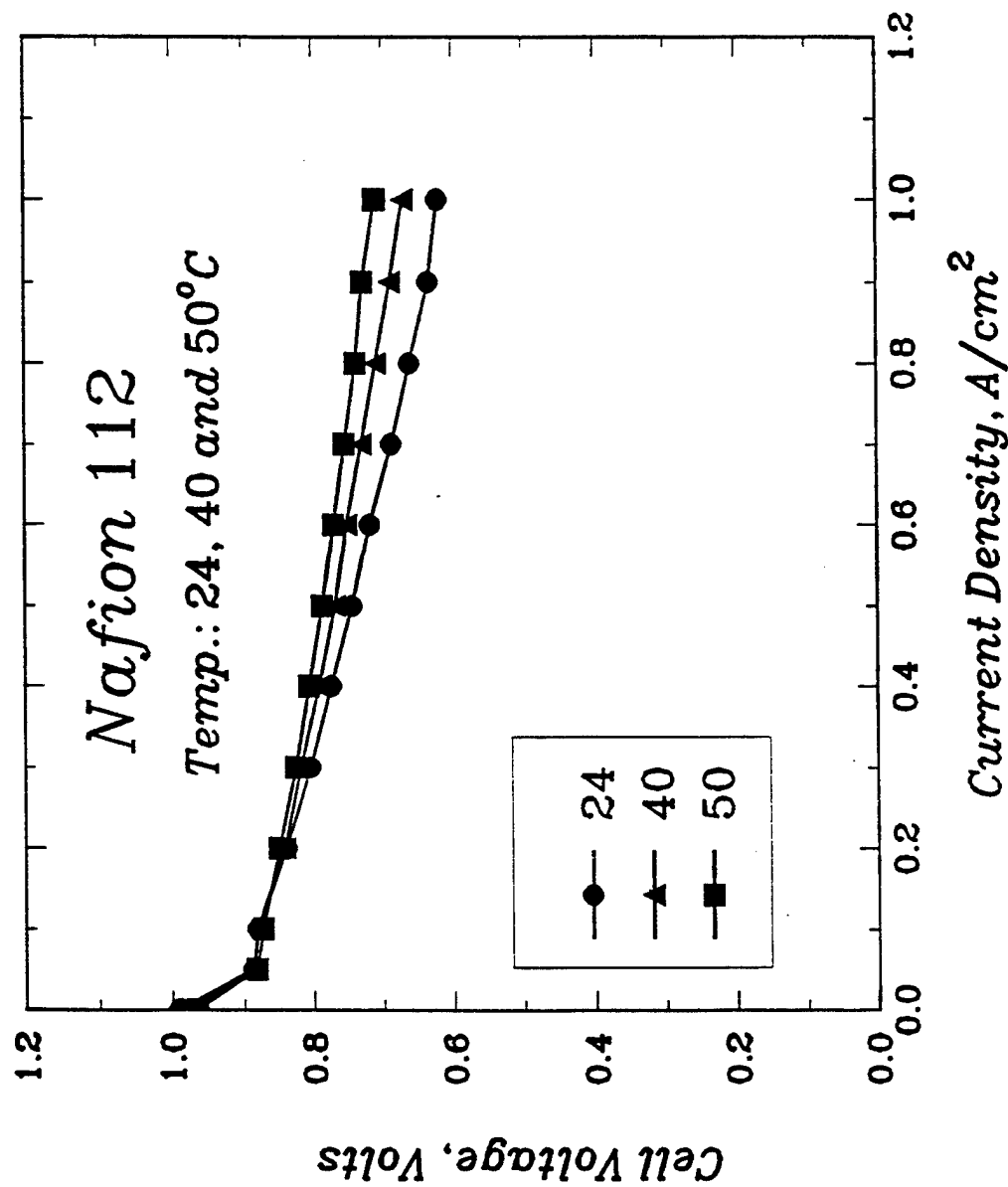
- In-house materials-oriented 6.1/6.2 R&D

- D-650 Program (supported by Army Materials Command)

- SBIR Program

- Contractual Programs (DuPont and JPL (E. Yen))

- CRDAs Program with CECOM (north) and H-Power corp.
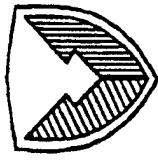
DIRECT ENERGY AND POWER DIVISION
US ARMY RESEARCH LABORATORY
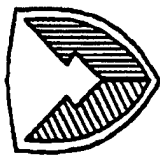
Hydrogen-fueled Fuel Cell Research and Development Program

- In-house materials-oriented 6.1/6.2 R&D

- D-650 Program Supported by Army Materials Command

- SBIR Program

- Contractual Programs (Du pont and JPL (E. Yen))

- CRDAs Program with CECOM and H-Power corp.

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Hydrogen-fueled Fuel Cell Research and Development Program

In-house materials-oriented 6.1/6.2 R&D

Objective: Improve state of the art PEM fuel cells for individual soldier systems and battery charger applications by providing better materials/components/designs at a lower cost

Fuel cell stack power in the 50-150 watts range for soldier system in support of CECOM's current development goals

Approach: Improve electrode/electrolyte interface

Develop lightweight monopolar cell stack concepts and novel materials
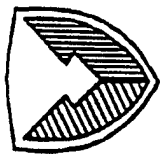
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Hydrogen-fueled Fuel Cell Research and Development Program

In-house materials–oriented 6.1/6.2 R&D

Nafion 117, 115, 112, 105

Temp: 50°C

●	117
▲	115
■	112
◆	105

Cell Voltage, Volts

Current Density, A/cm²

Hydrogen-fueled Fuel Cell Research and Development Program

In-house materials- oriented 6.1/6.2 R&D

Nafion 112

Temp.: 24, 40 and 50°C
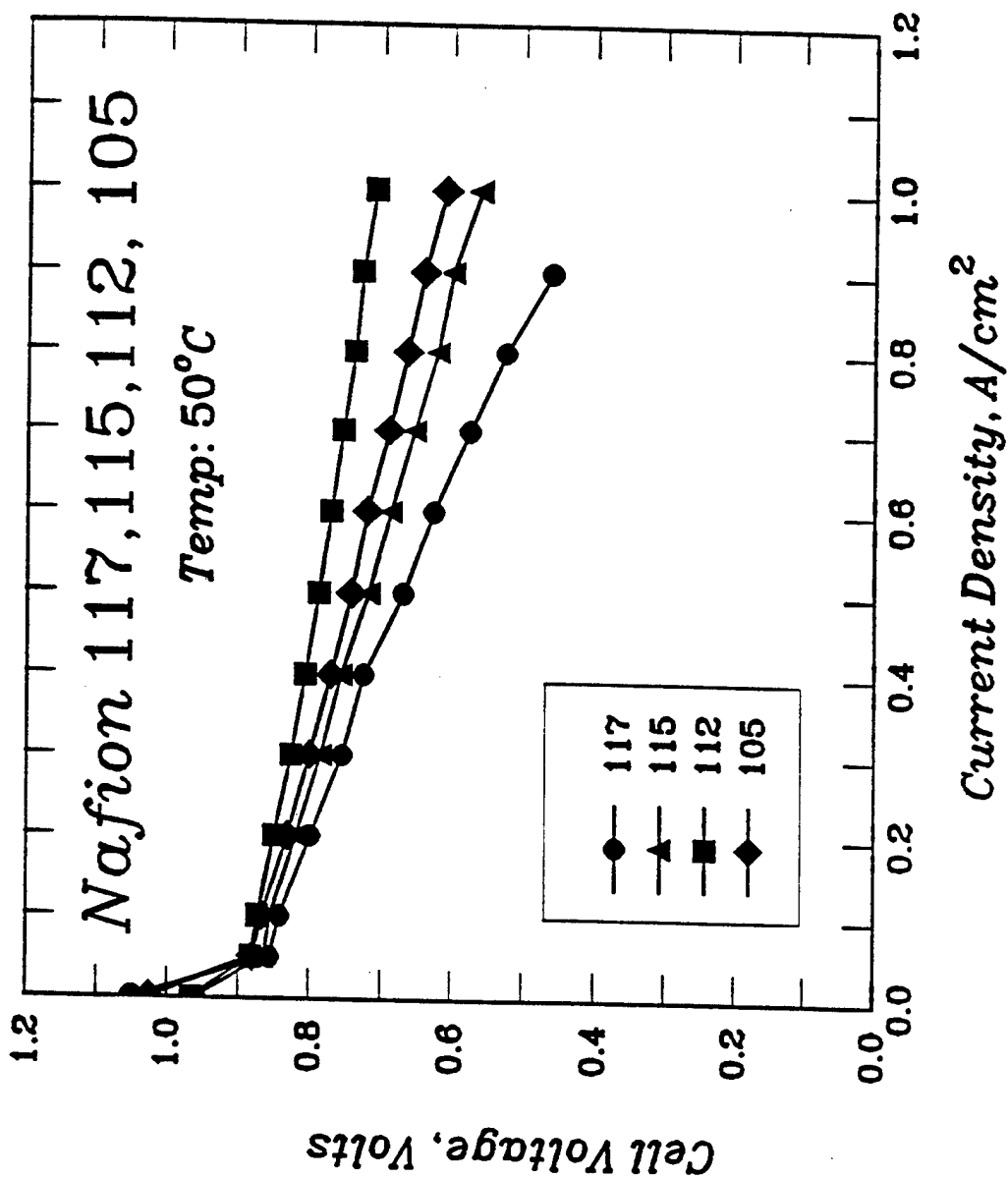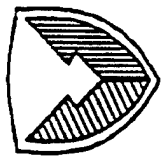
Hydrogen-fueled Fuel Cell Research and Development Program
In-house materials-oriented 6.1/6.2 R&D

lightweight monopolar cell stack design

(U. S. patent pending Serial No. 08/320611 field 10/6/94 R. Mammone, M. Binder and S. Gilman)
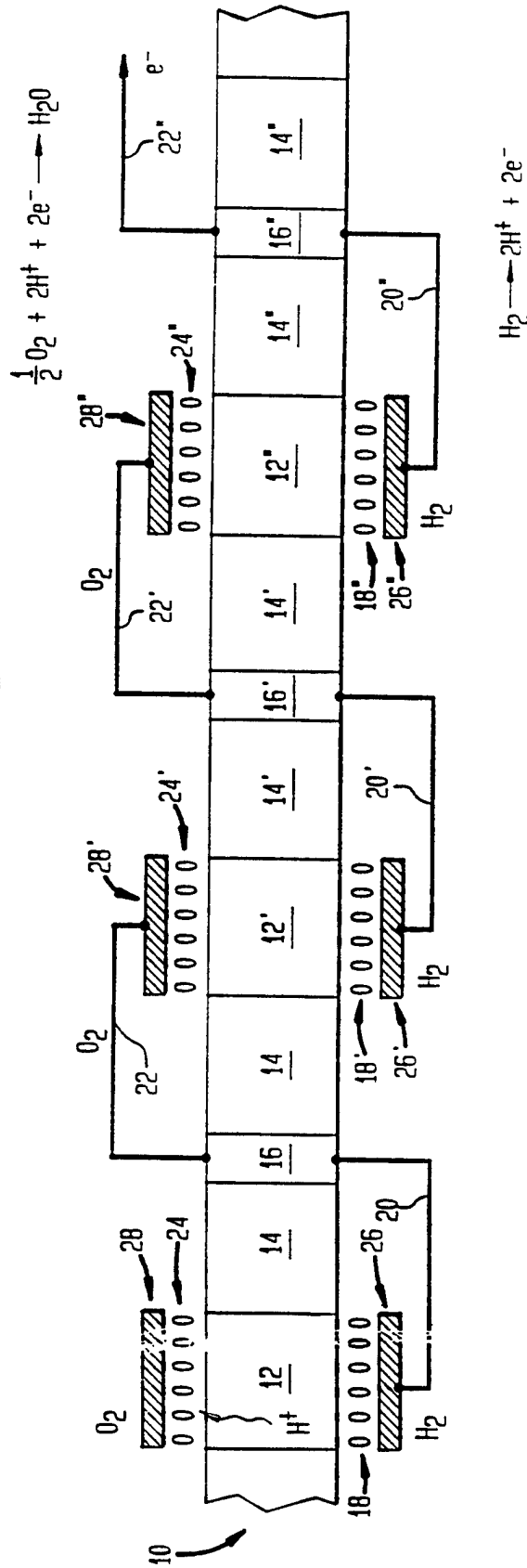
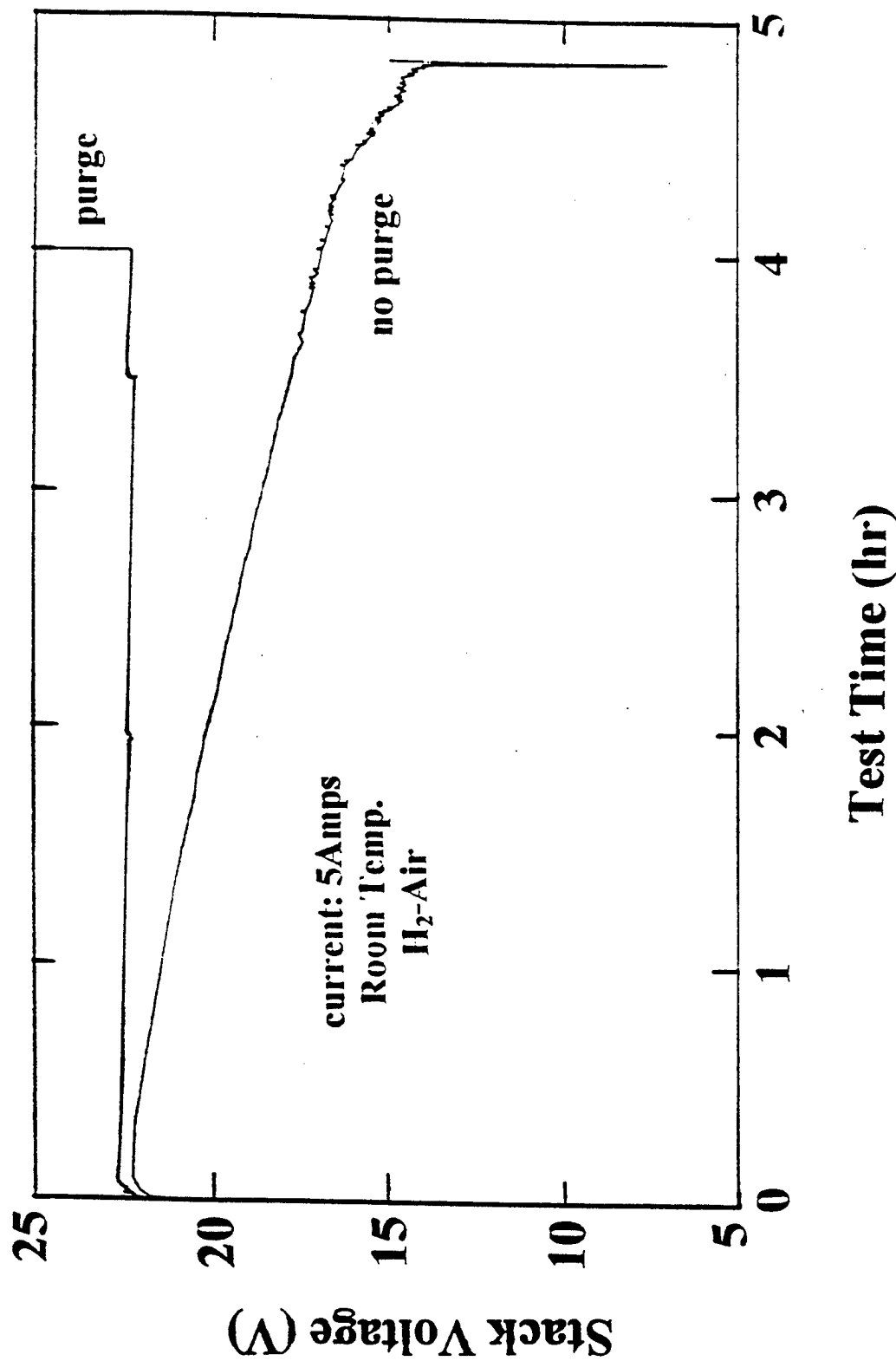$$\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O$$

$$H_2 \longrightarrow 2H^+ + 2e^-$$

FIG. 1

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Hydrogen-fueled Fuel Cell Research and Development Program

- In-house materials-oriented 6.1/6.2 R&D

- **D-650 Program**

- SBIR Program

- Contractual Programs (Du pont and JPL (E. Yen))

- CRDAs Program with CECOM and H-Power corp.

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Hydrogen-fueled Fuel Cell Research and Development Program

D-650 Program

Objective: To evaluate PEM fuel cells stack and system performance

Status:

- 25 watts air-breath Fuel Cell Stack
- 100 watts air-pumped Fuel Cell Stack
- Ballard will deliver a 100 watts fuel cell system to ARL on Sept. 97

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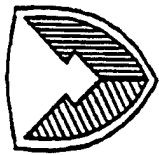
Hydrogen-fueled Fuel Cell Research and Development Program

D-650 Program

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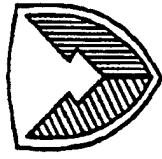## US ARMY RESEARCH LABORATORY

Hydrogen-fueled Fuel Cell Research and Development Program

- In-house materials-oriented 6.1/6.2 R&D

- D-650 Program Supported by Army Materials Command

- **SBIR Program**

- Contractual Programs (DuPont and JPL (E. Yen))

- CRDAs Program with CECOM and H-Power corp.

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US ARMY RESEARCH LABORATORY
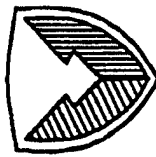
Hydrogen-fueled Fuel Cell Research and Development Program

SBIR Program: Lightweight PEM Fuel Cell Stack Development

Objective: To develop lightweight monopolar or bipolar hydrogen-fueled stacks using novel materials and designs

Fuel cell stack power in the 50-150 watts range for soldier system in support of CECOM's current development goals

Status:

- 11 SBIR Phase I contracts ($ 70 K each) have been completed
- 3 SBIR Phase II Programs ($600 k for 2 year Program) in PEM Fuel Cells awarded.

Deliverables include a 50W and 150W PEM Fuel Cell Stacks.

Contractors:

Analytical Power Corp., Lyntech Inc. , and MER corp.

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Hydrogen-fueled Fuel Cell Research and Development Program

- In-house materials-oriented 6.1/6.2 R&D

- D-650 Program Supported by Army Materials Command

- SBIR Program

- Contractual Programs (Du pont and JPL (E. Yen))

- CRDAs Program with CECOM and H-Power corp.

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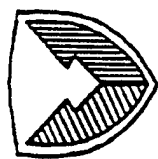# DIRECT ENERGY AND POWER DIVISION
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Hydrogen-fueled Fuel Cell Research and Development Program

Contractual Programs

- Jet Propulsion Laboratory (E. Yen, JPL)
  Synthesized and evaluated membranes based on the Sulfonic Acid Salt
  of Poly(P-Phenylene-ether sulfone) [PES] and the Sulfonic Acid Salt of
  Poly(ether-ether ketone) [PEEK]

- DuPont
  Synthesized and characterized Nafion membrane made from lower
  equivalent weight resins, Studied effects of crosslinking Nafion by
  electron Beam irradiation of Nafion in the presence of various monomers
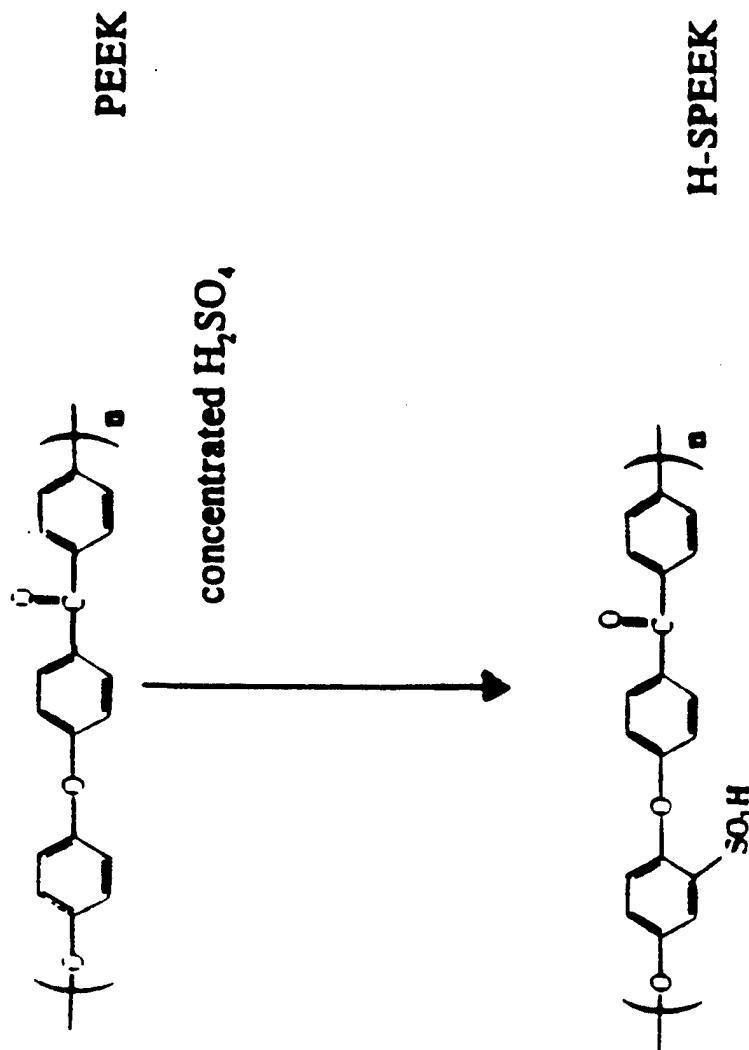
45

DIRECT ENERGY AND POWER DIVISION
US ARMY RESEARCH LABORATORY

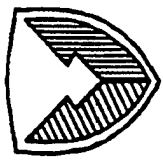Hydrogen-fueled Fuel Cell Research and Development Program

Contractual Programs

Jet Propulsion Laboratory (E. Yen, JPL)

PEEK

concentrated H_2SO_4

H-SPEEK

SO_3H

DIRECT ENERGY AND POWER DIVISION
US ARMY RESEARCH LABORATORY

Hydrogen-fueled Fuel Cell Research and Development Program
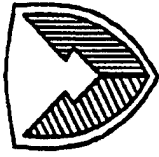
Contractual Program
DuPont

Approaches:

- Use of low equivalent weight monomer
- Use of irradiation (with/without) added reagents to introduce functional groups and to induce cross-linking
- Measure conductivity, water absorption
- Construct/evaluate small fuel cells

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Hydrogen-fueled Fuel Cell Research and Development Program

- In-house materials-oriented 6.1/6.2 R&D

- D-650 Program Supported by Army Materials Command

- SBIR Program

- Contractual Programs (Du pont and JPL (E. Yen))

- CRDAs Program with CECOM and H-Power corp.

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Hydrogen-fueled Fuel Cell Research and Development Program

CRDAs Program with CECOM (North)

SINCGARS Testing Profile

1. Transmit load: 20 watts, 1 minute
2. Receive load: 6 watts, 9 minutes
3. Nominal battery potential: 15 V
4. End of life potential: 9 V
5. Testing regime is a cyclic profile of 1 min transmit (20 W) followed by 9 min receive (6 W). This cycle regime is then continued until a 9 V cutoff is reached.

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Direct Methanol Fuel Cell Research and Development Program

Methanol/PEM fuel cells offer the possibility for relatively simple,small, and high energy systems

Objective: Improve overall performance in direct methanol PEM fuel cell

Status:
- In-house materials-oriented 6.1
- Microelectrons Research Cooperative Program (MRCP) with Johns Hopkins University

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US ARMY RESEARCH LABORATORY

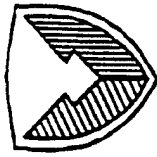**Direct Methanol Fuel Cell Research and Development Program**

In-house materials-oriented 6.1

Internal work has been oriented toward electrocatalyst characterization

- Searched for more efficient catalysts for methanol electro-oxidation
- Investigated continuous series of Pt-Ru methanol oxidation catalysts
- Identified optimal compositions and mechanism
- Methanol-Oxygen interaction at a Pt-rotating disk electrode
- Methanol "cross-over" to the cathode

- Develop new methanol-tolerant electrocatalysts for the cathode
- Investigate electrode/electrolyte interface effects on methanol crossover

DIRECT ENERGY AND POWER DIVISION
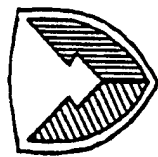# US ARMY RESEARCH LABORATORY

Direct Methanol Fuel Cell Research and Development Program
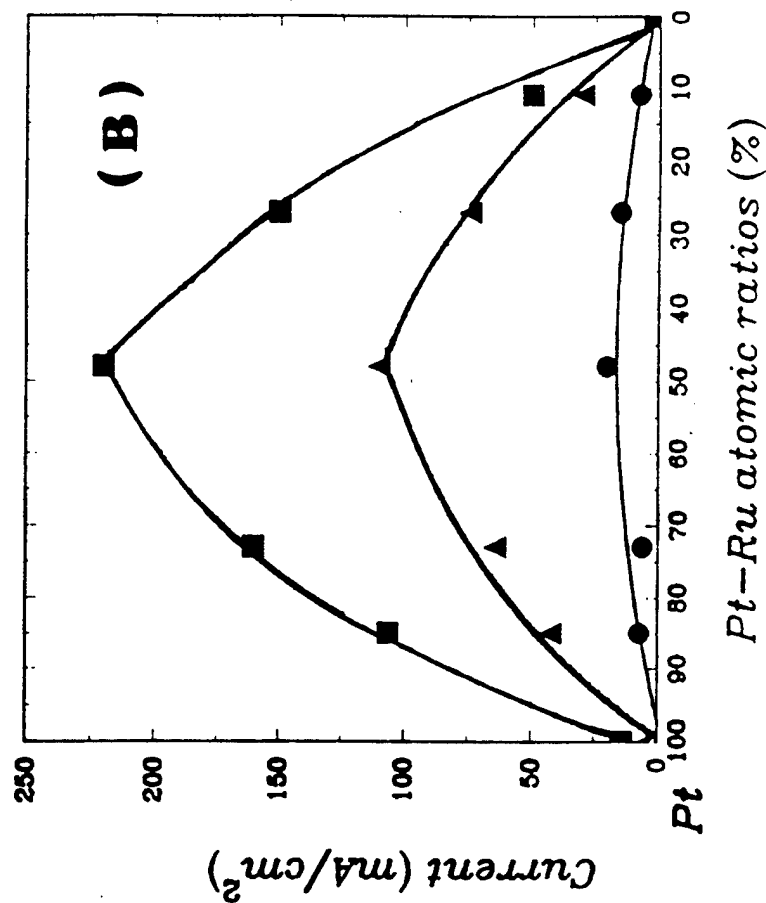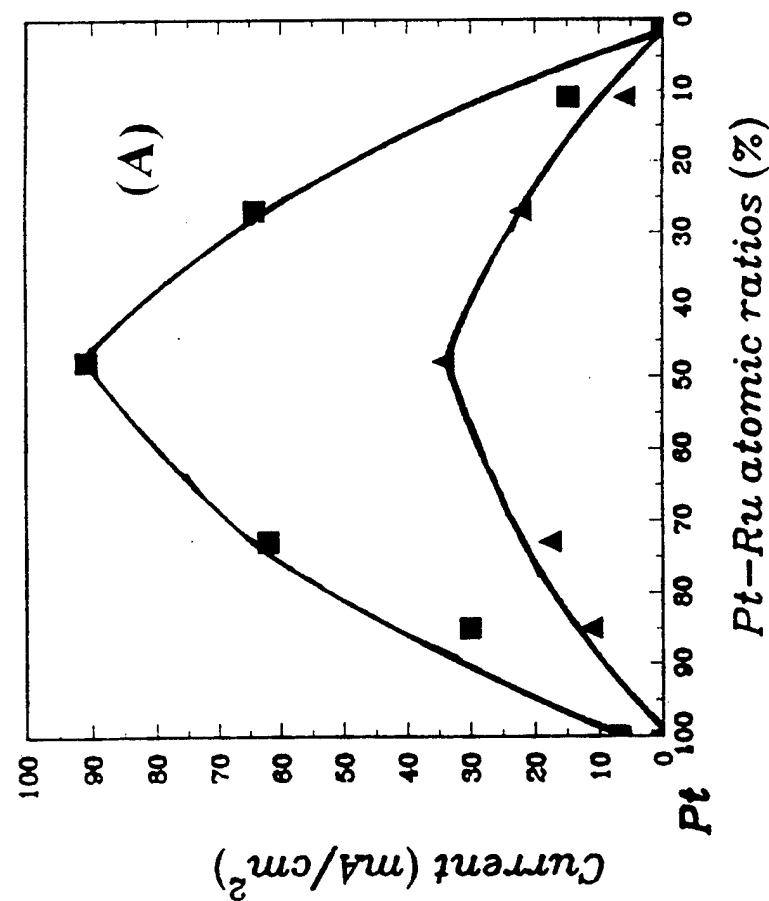Investigated continuous series of Pt-Ru methanol oxidation catalysts
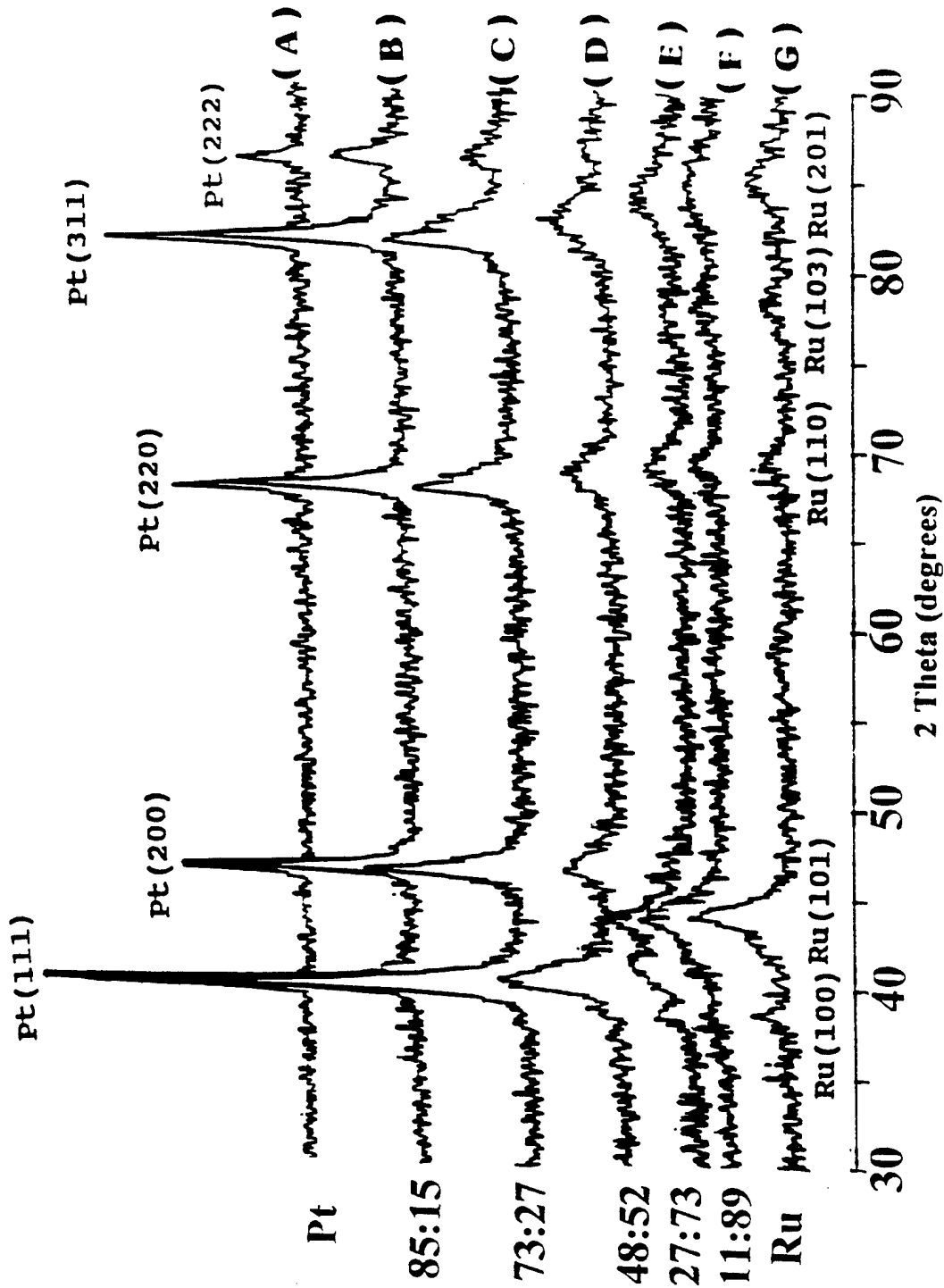
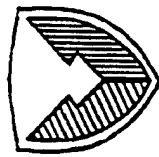# DIRECT ENERGY AND POWER DIVISION
US ARMY RESEARCH LABORATORY

Direct Methanol Fuel Cell Research and Development Program
Identified optimal compositions

DIRECT ENERGY AND POWER DIVISION
US ARMY RESEARCH LABORATORY

Direct Methanol Fuel Cell Research and Development Program

Identified methanol electro-oxidation mechanism

"Bifunctional Catalyst Mechanism"

$$CH_3OH_{sol} \Longleftrightarrow CH_3OH_{ads.} \Rightarrow Pt\text{-}CO_{ads.} + 4\,H^+ + 4\,e^-$$

$$Ru + H_2O \Longleftrightarrow Ru\text{-}OH_{ads} + H^+ + e^-$$

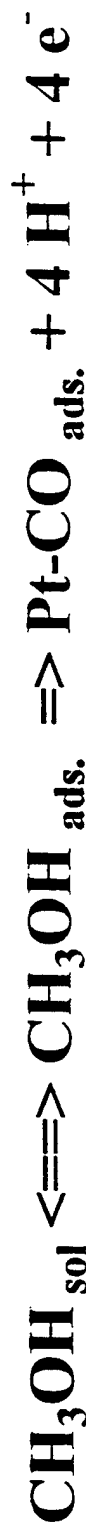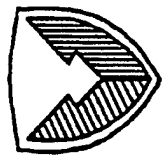$$Pt\text{-}CO_{ads.} + Ru\text{-}OH_{ads.} \Longleftrightarrow CO_2 + H^+ + 4e^-$$

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Direct Methanol Fuel Cell Research and Development Program

BET Surface Areas and Particles Size of
Unsupported Pt-Ru Alloy Electrocatalysts

Composition of Pt-Ru alloy	Bet surface area (m^2/g)	Particle size diameter $(\mathring{A})$
Pt:Ru (85:15)	4.7	615
Pt:Ru (73:27)	12.5	239
Pt:Ru (48:52)	21.8	151
Pt:Ru (27:73)	27.7	133
Pt:Ru (11:89)	27.5	154

$$SA_{BET} = 6/D_s \, \rho_{(Pt+Ru)}$$

ρ: alloy density $[\rho_{(Pt+Ru)} = w/o \, Pt \, x \, \rho_{pt} + w/o \, Ru \, x \, \rho_{Ru}]$

DIRECT ENERGY AND POWER DIVISION
US ARMY RESEARCH LABORATORY
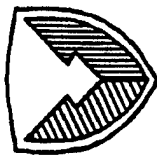
Direct Methanol Fuel Cell Research and Development Program
Methanol-Oxygen interaction at a Pt-rotating disk electrode

(A): 0.5M H_2SO_4 Sat. N_2
with 1M CH_3OH

(B): 0.5M H_2SO_4 Sat. O_2
with 1M CH_3OH

(C): 0.5M H_2SO_4
Sat. with O_2

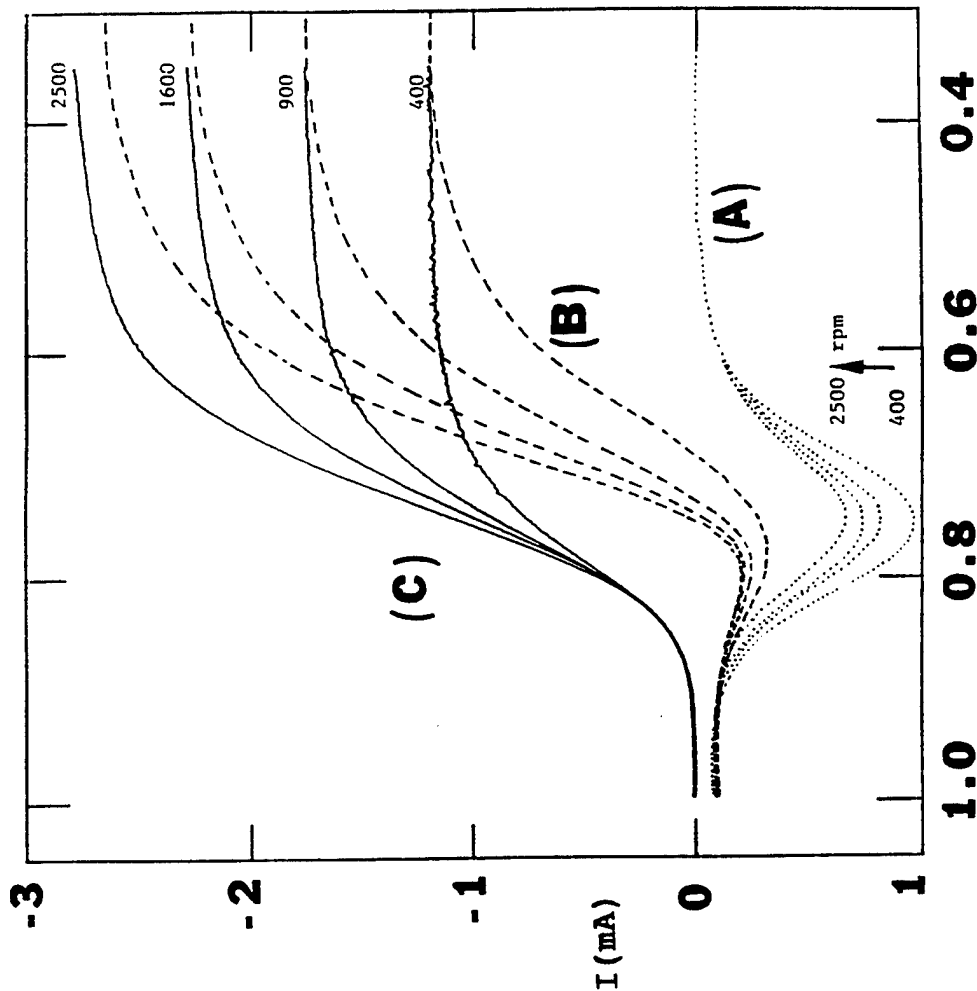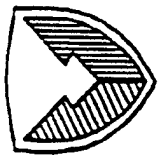**Direct Methanol Fuel Cell Research and Development Program**
Methanol-Oxygen interaction at a Pt-rotating disk electrode
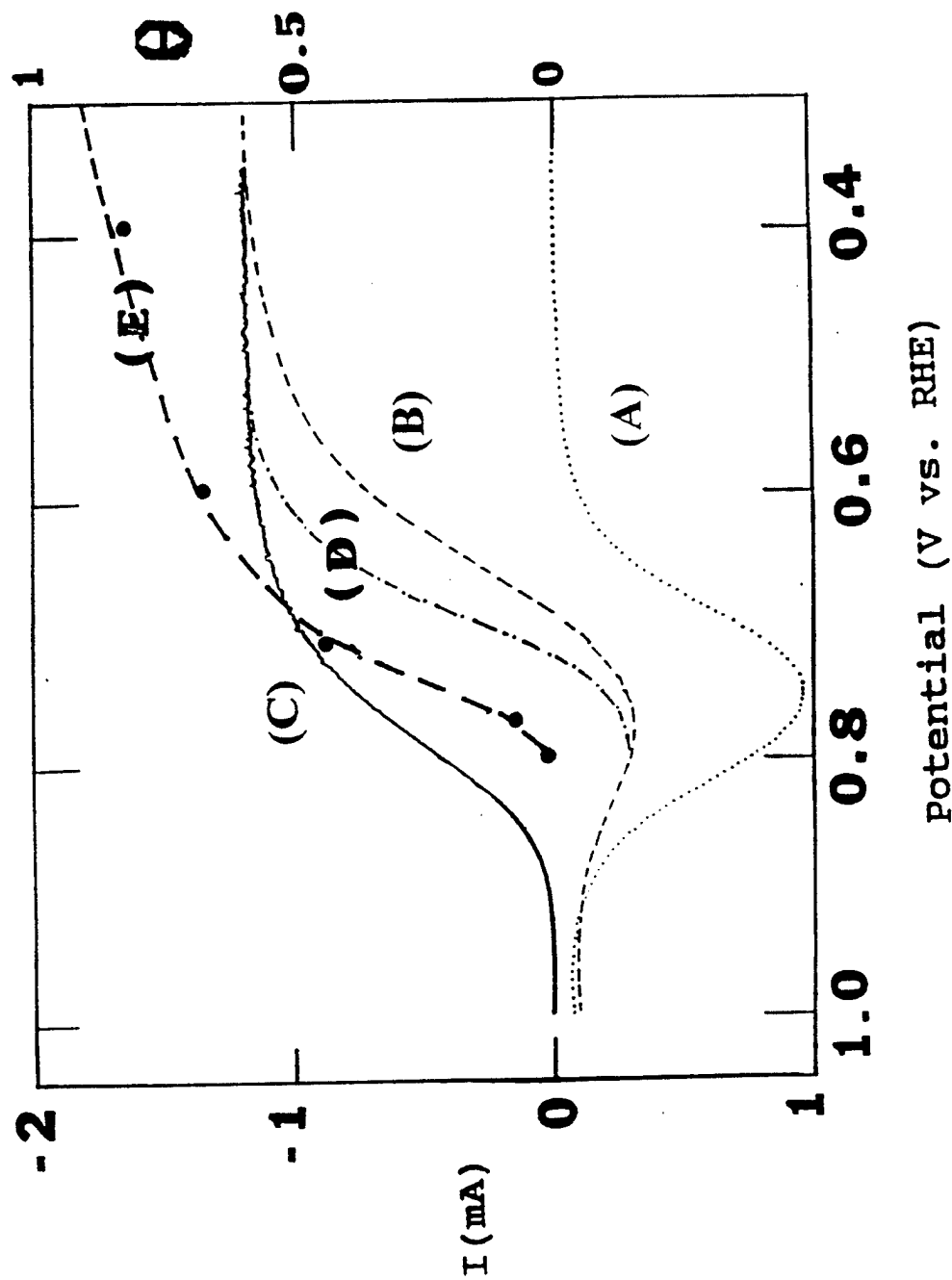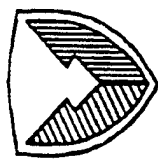
Direct Methanol Fuel Cell Research and Development Program
Methanol "cross-over" to the cathode for a single fuel cell
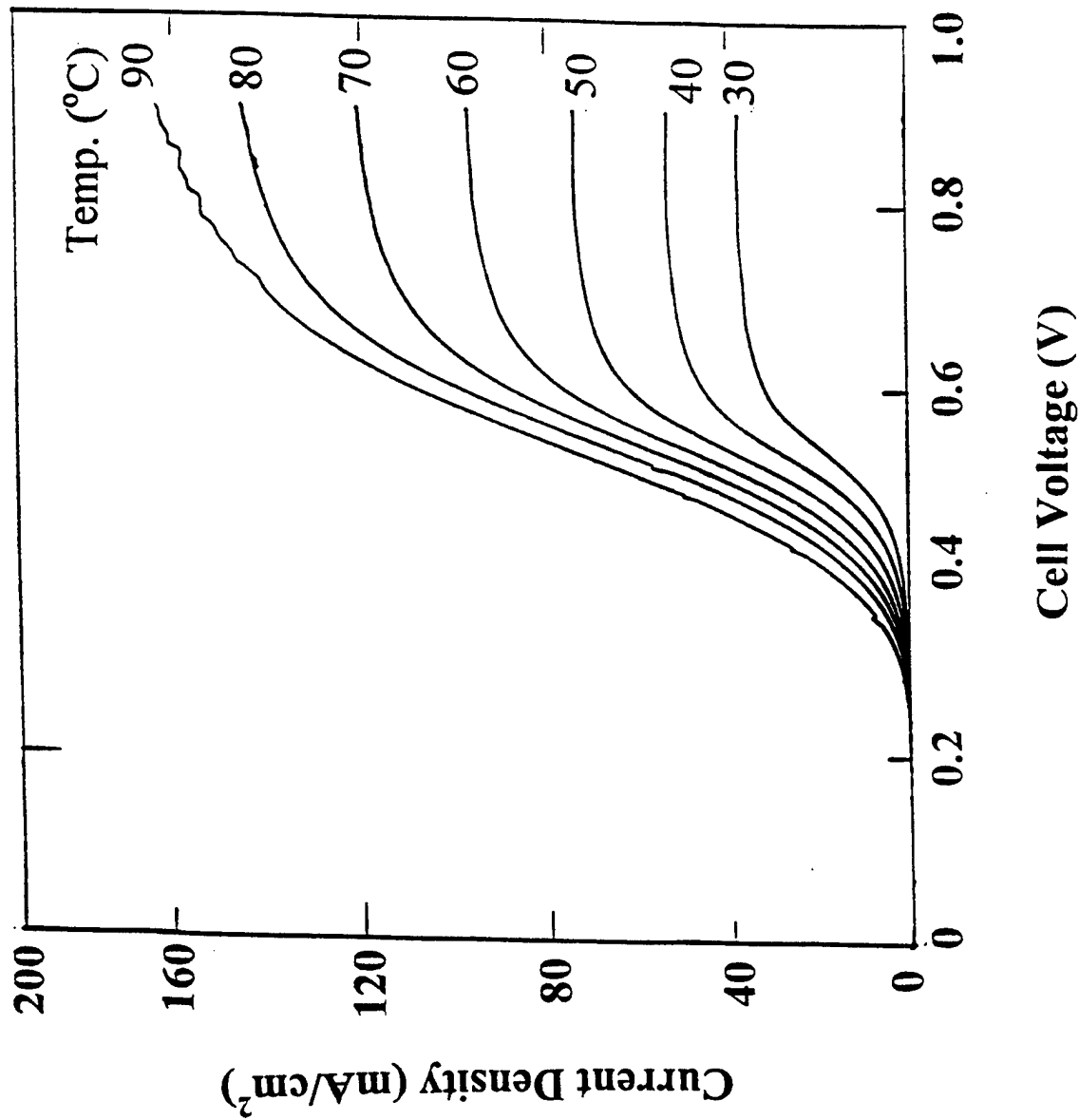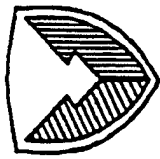
Direct Methanol Fuel Cell Research and Development Program

MRCP with Johns Hopkins University

(I) Electrocatalyst

• Surface preparation and bulk alloy processing of Pt and Pt-Ru alloys and to determine the real surface areas of Pt-Ru electrocatalyst

• Searches for more efficient electrocatalysts

(II) Membrane

• Prepares new membrane electrolyte with lower methanol "cross-over" rate

DIRECT ENERGY AND POWER DIVISION
US ARMY RESEARCH LABORATORY
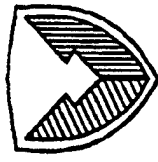
Overview of ARL Fuel Cells Research and Development Program

97.2 Army SBIR topic title: "Innovative Fuel Cells"

- Use of alternate fuels

  e.g. methanol, ammonia, hydrocarbons

- Design of novel fuel storage/delivery systems

  e.g. lightweight hydrogen generators

- Substitution of lightweight/less costly/more efficient materials

  e.g. new/composite PEM, improved/novel catalysts

SYSTEM CONSIDERATIONS

PRESENTED TO:

WORKSHOP ON HYDROGEN STORAGE
AND GENERATION FOR MEDIUM -
POWER AND -ENERGY APPLICATIONS

James K. "Jay" Stedman

April 8, 1997

Discussion Topics

- System Optimization Factors
- Thermals and Heat Transfer
- Water Balance
- System Integration
- Environmental Factors
- Hydrogen Conditions and Logistics

System Optimization

- Power & Energy Requirements
- Optimization Criteria
- Hydrogen Storage Mode

Power & Energy Requirements

- a. 300 watts for 33 hours
- b. 100 watts for 10 hours
- c. 10 watts for 1 year
- Implications:
  - * simple systems (especially c.)(conventional thinking)
  - * a. & b.-many starts,easily refueled,user friendly
  - * c.-remote operation, special everything OK

Optimization Criteria

- **Weight and Volume Vs. Efficiency**
  - ❋ Single or Multiple Missions
- **Cost**
  - ❋ Materials Cost and Production
- **Reliability and Life**
  - ❋ Operating Stress
  - ❋ Redundancy
  - ❋ Weight, Volume, Cost

Hydrogen Storage Mode

- Subject of Workshop

- If Need Heat-Use What's Available

- If Exothermic-Combine With Endothermic

- Consider Safety of Chemical Hydrides

- Consider Refueling of Gas Tanks

- Consider Flexibility of Load Profile and Mission Duration

Thermals and Heat Transfer

- Endothermic/Exothermic and Quantity
- Temperature Limits on Reaction
- Environment Temperature Range
- Heat Transfer Medium
- Power Turndown

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Water Management Issues

- H2 Source Stoichiometry - Moles of H_2O Consumed/Moles H_2O Produced by Fuel Cell

- Water Addition to Source- Form and Control

- Water Recovery Hardware and Control

  * Environmental Temperature Limits

  * Fuel Cell Operating Conditions

  * Weight and Volume Could Be Significant

System Integration

- **Higher Efficiency from Thermal Integration**
  - * vaporization--condensation
  - * vapor transfer for humidification
  - * heat rejection--adsorption

- **Electrical Control-Power Conditioning**
  - * same box
  - * common elements

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System Intergration

- **Up Transients with H2 Generators**
  - * Storage
    - * gaseous
    - * metal hydride
  - * Battery/Capacitor
- **Down Transients**
  - * Thermal mismatch problem

Environmental Factors

- **Temperature Limits = -25 to + 125F**
  - Fuel cells make water (water freezes at 32F)
    - Do your Best
- **Shock & Vibration**
  - real requirements
  - testing required
- **Battlefield Air-What is it?**
- **Orientation-+/- 45 °**

User Considerations

- small fuel cells compete with lithium batteries–special fuel OK

- logistics a concern, especially for the foot soldier application

- need to offer significantly better performance to gain acceptance of new concept.

Required Hydrogen Characteristics

- Pressure- Slightly Over One Atmosphere

- Humidity-for missions a. & c. non required, for b., maybe (HPD)

- Purity-need testing: data shows Ca, Mg,i.e., bivalent metals reduce membrane conductivity. Dust, soot, etc-also bad.

- . For short missions ?? Don't do anything heroic until testing shows a need.

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DARPA Hydrogen Storage Programs

April 8-10, 1997

Hydrogen Storage and Generation Technologies Workshop

Roger Pyon

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DARPA Program Objectives

- Development of high energy density (by weight and volume) hydrogen storage sources.

- Applications

  - Field Portable Power
  - Land Vehicles
  - Remote Sites
  - Unmanned Undersea Vehicles

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Current Programs

Small Business Innovative Research (SBIR) phase 2 efforts

- A. F. Sammer - Chemical Hydride

- Energy Conversion Devices - Metal Hydride

- Materials & Electrochemical Research - Fullerene Hydride

A. F. Sammer Technology Description
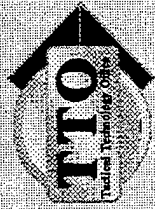
Objective

- Development of a chemical hydride hydrogen storage/generation system

Approaches

- Hydrogen generation by reaction of CaH_2 & LiH with water
- Replaceable hydride cartridges
- Load responsive

Status

- 50 and 100 L chemical hydride generator demonstrated
- Hydrogen delivery rate of 10 to 250 ml per minute (Designs available which would provide upto several L/min and/or 10,000 L capacity)
- 100 L CaH_2 system provides 167 Whrs @ single cell voltage of 0.7 V
- The complete 100 L system weighs 1 kg and has a volume of 0.92 L
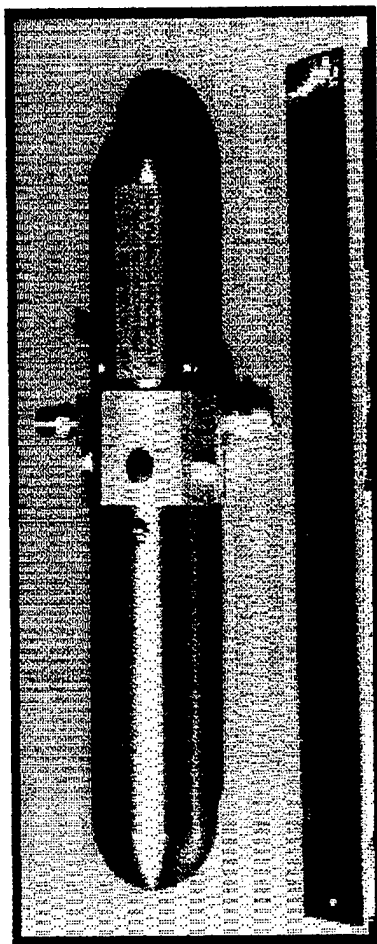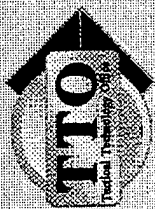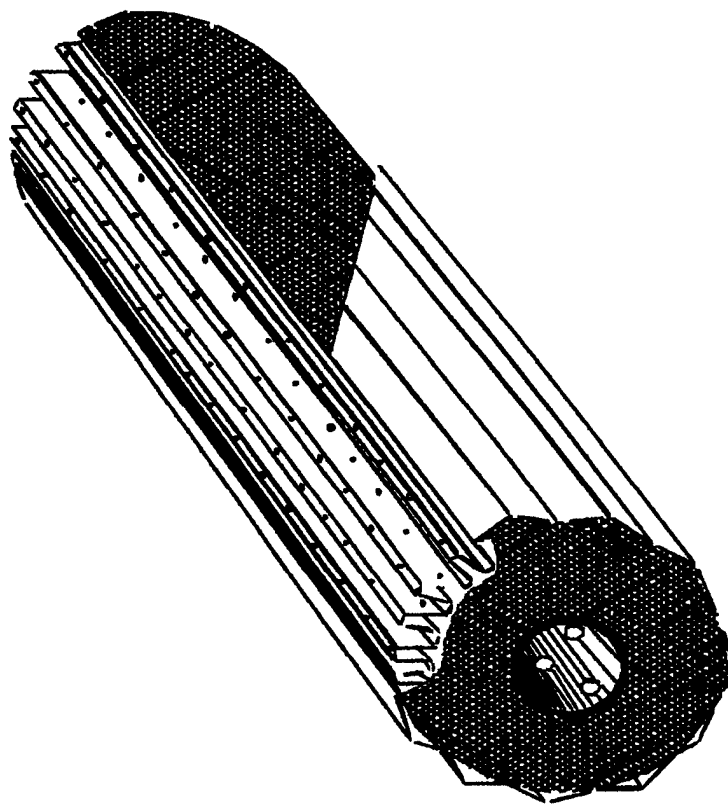
Hydride cartridge cut-away

100 L Generator

4/08/97

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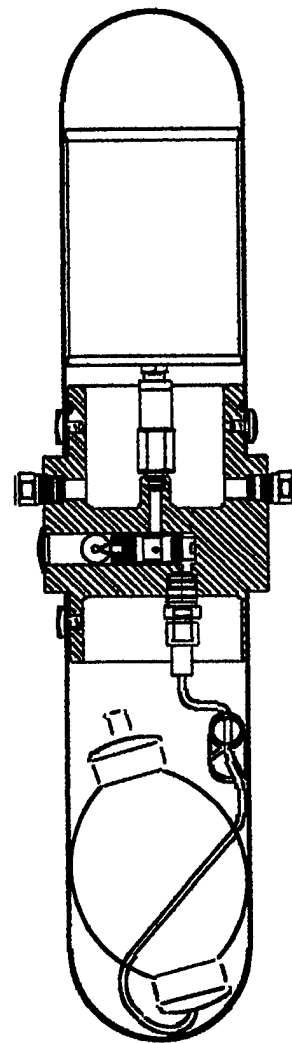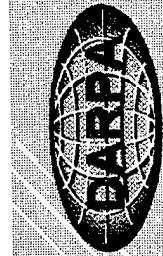
ECD Technology Description
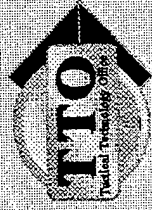
Objective

- Development of a metal hydride hydrogen storage/generation system

Approaches

- Magnesium based alloys for the storage of hydrogen in the form of metal hydrides
- Demonstration of low adsorption and desorption temperatures

Status

- Magnesium based alloy with hydrogen storage capacity of 5-6 wt. % demonstrated
- Hydrogen formation at 100 °C and desorption at 250 °C
- Over 2000 adsorption/desorption cycles demonstrated on a 5 gram sample
- Reported alloy yield of 50%
- Resistant to CH_4 and CO poisoning

4/08/97

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MER Technology Description

Objective

- Development of hydrogen storage/generation system in fullerene structures

Approaches

- Reversible chemical absorption and desorption of fullerenes
- Physical hydrogen gas adsorption on tubular fullerenes at cryogenic temp and desorption at room temp
- Use of catalyst to reduce activation energy required in absorption and desorption process

Status

- Chemical hydrogenation of fullerenes
  - 5.7 wt. % in solid state
  - 6.9 wt. % in liquid state at 180 °C and 500 psi
- Chemical de-hydrogenation
  - Solid state de-hydrogenation achieved with catalyst but requires high temperature and pressure
  - Liquid state de-hydrogenation is limited by the choice of solvents

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Pressurized Hydrogen Storage

8-10 April 1997

Workshop on Storage and Generation of Hydrogen

Prepared By:

Brian D. James
4001 N. Fairfax Drive, Suite 775
Arlington Va 22203
(703) 243-3383 voice
(703) 243-2724 fax

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Comparison of Tank Performance Factors ($P_{burst} * V_{internal}/W_{tank}$) for Various Materials

Performance Factor [in]

(Burst Pressure [psi]) * (Volume [in³]) / (Tank Weight [lb])

All data except "Graphite/Bladder" have been extracted from Figure 4 of the Feasibility Study of Onboard Hydrogen Storage for Fuel Cell Vehicles (Interim Report), DOE, January 1993

IDEAL

DOE/Ford T1000G

DOE/Ford T700S

Graphite/Bladder
Graphite/Plastic
Graphite/Aluminum
Aramid/Aluminum
S-Glass/Aluminum
E-Glass/Aluminum
Titanium
Aluminum
Steel

2,500,000
2,000,000
1,500,000
1,000,000
500,000
0

Mitlitsky-FC_Seminar-961120-13

FM930402/NJC

A Bladder Was Fabricated Which Held Adequate Pressure for Use as an Inflatable Mandrel

A Lightweight Bladder Was Used as an Inflatable Integral Mandrel for Fabricating a Pressure Vessel

Final composite layer wound onto vessel

First Prototype with Rex Haddock and Fred Mitlitsky

Inflated bladder on winding axis
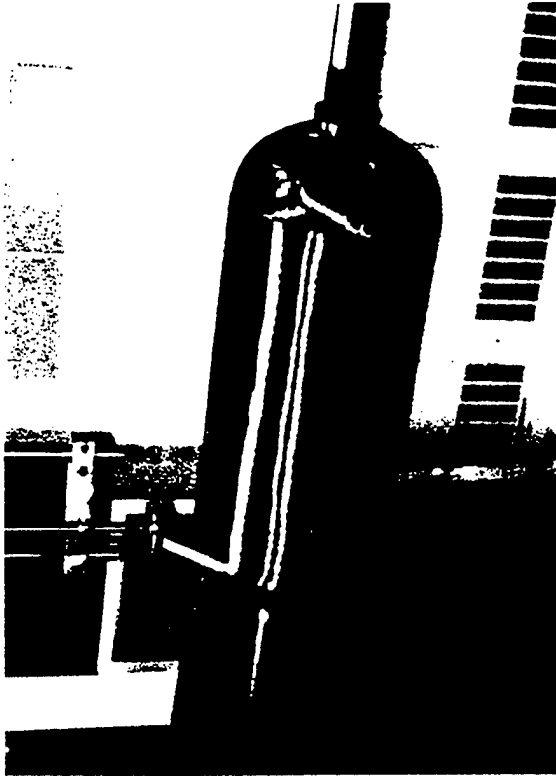
First composite layer wound onto bladder

Hydrogen Density at 300K (81°F)

DIRECTED TECHNOLOGIES, INC.

Hydrogen Density (lbm/ft3)

Hydrogen Pressure (psia)

DIRECTED TECHNOLOGIES, INC.
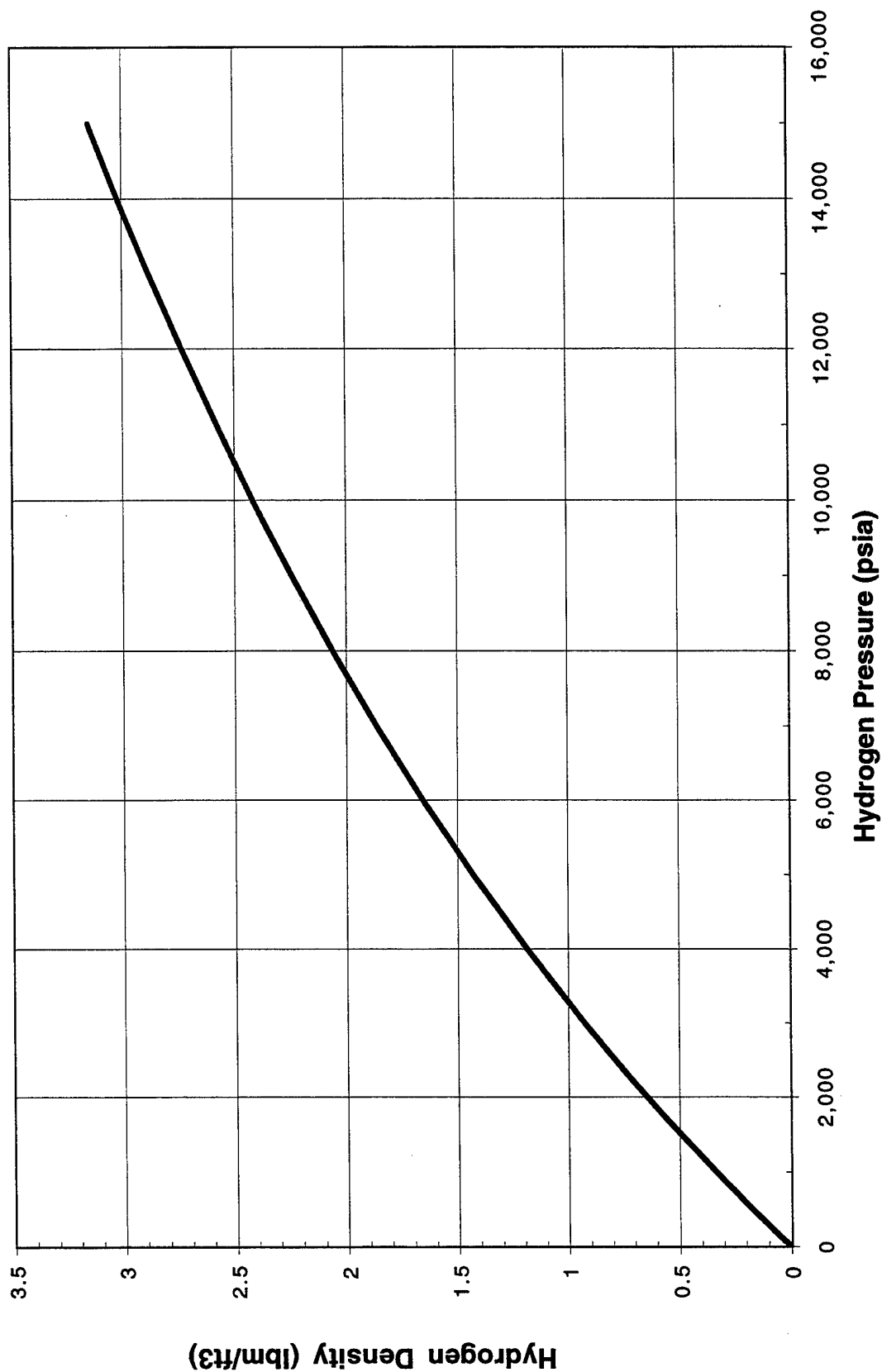
Hydrogen Pressure Tankage Assumptions

H2 Storage:

1 kWh	=>	0.05270 kg (0.1162 lbs) H_2
5 kWh	=>	0.2635 kg (0.5810 lbs) H_2
10 kWh	=>	0.5270 kg (1.162 lbs) H_2
45 kWh	=>	2.372 kg (5.23 lbs) H_2
90 kWh	=>	4.744 kg (10.46 lbs) H_2

Based on 0.7 volts per cell in PEM fuel cell with no parasitic loads i.e. 57% lower heating value (LHV) system efficiency

Operating Pressure:
34.5 MPa (5,000 psia)
51.8 MPa (7,500 psia)
69 MPa (10,000 psia)
103.5 MPa (15,000 psia)

Safety Factor (Burst Pressure/ Operating Pressure) = 1.5 and 2.25

Fiber and Resin:
T-1000G carbon fiber
Ultimate tensile strength 6.37 Gpa (924 ksi) derated to 81% to account for variability in fibers and manufacturing
Fiber density = 1.8 g/cc
Resin density = 1.2 g/cc
Fiber volume fraction = 58%
Performance Factor for fibers/resin alone = 2.3 X 10^6 inches
Performance Factor = (Operating Pressure X Safety Factor X Internal Volume)/ (tank weight)
10% additional fiber and resin weight to approximate fiberglass overwrap for abrasion and impact resistance

**Tank Liner (gas barrier):** metalized 5 mil thick composite of LDPE and PET

Tank Internal Length to Diameter Ratio = 3

Boss Weight (total):
0.24 kg (0.52 lbs) for 1 kWh, 5 kWh, and 10 kWh systems based on Al construction, 6 inch diameter plate with 2 inch diameter port
0.46 kg (1.02 lbs) for 45 kWh and 90 kWh systems based on Al construction, 4 inch diameter plate with 1 inch diameter port

Pressure Reducer: 0.5 kg (1.1 lbs)

Flow Metering Assembly: 0.36 kg (0.8 lbs) total weight
Consists of: piezo-electric valve
DC-DC converter
small battery

Hydrogen Storage Gravimetric Efficiency

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TECHNOLOGIES, INC.

5,000 psia
7,500 psia
10,000 psia
15,000 psia

T-1000G Carbon Fiber
Safety Factor = 1.5
Internal Length/Diameter = 3

18,970 Wh/kg H2 at 57% LHV system efficiency
(0.7 volts/cell and no parasitic losses)

Hydrogen Weight Percentage

Weight of Stored Hydrogen, kg
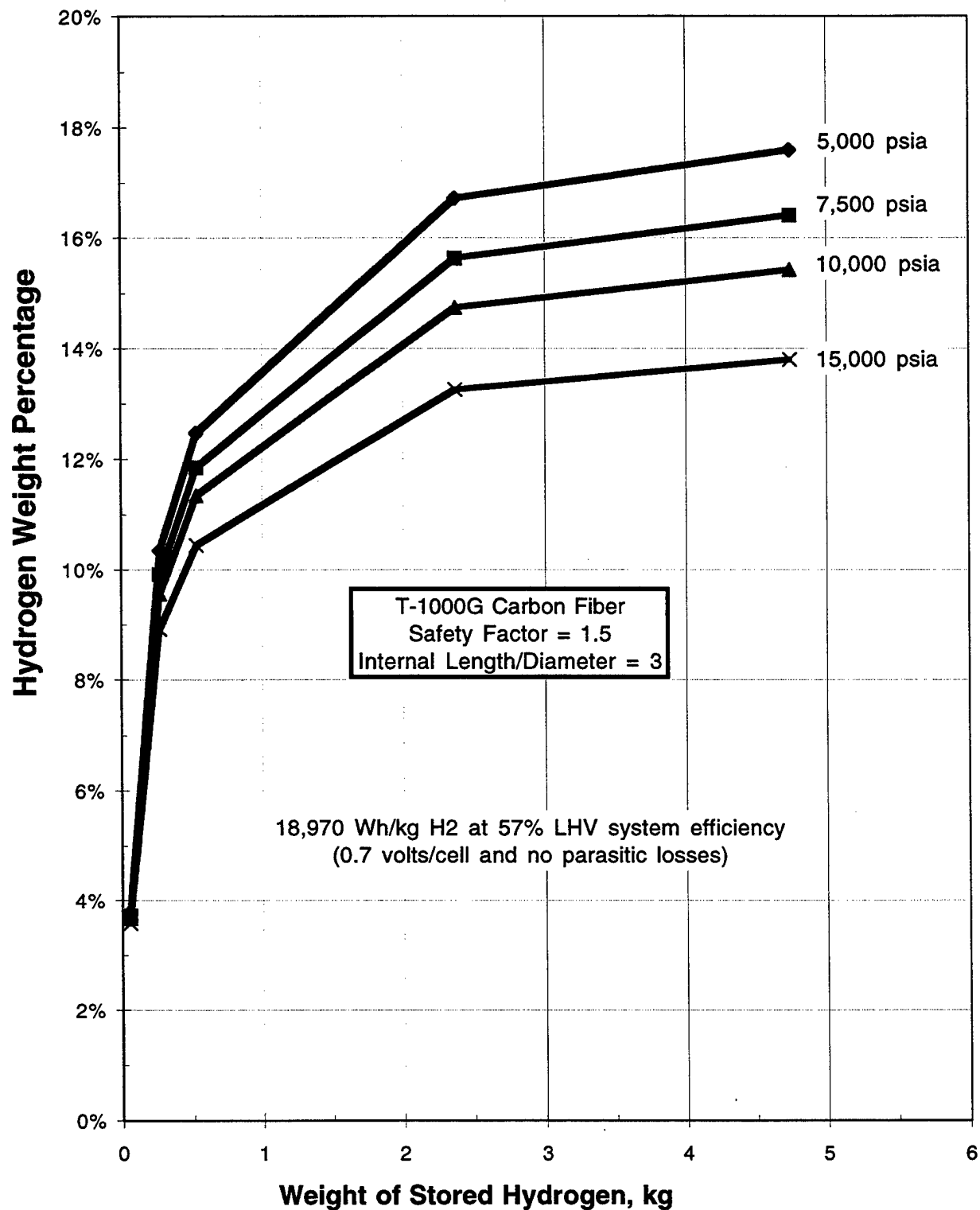
Hydrogen Storage Volumetric Efficiency

DIRECTED TECHNOLOGIES, INC.

Y-axis: Hydrogen Stored per System Volume, kg H2/system liter

X-axis: Weight of Stored Hydrogen, kg

15,000 psia
10,000 psia
7,500 psia
5,000 psia

T-1000G Carbon Fiber
Safety Factor = 1.5
Internal Length/Diameter = 3

18,970 Wh/kg H2 at 57% LHV system efficiency
(0.7 volts/cell and no parasitic losses)

Advanced Pressurized Hydrogen
Tankage System
(Safety Factor = 1.5)

DIRECTED TECHNOLOGIES, INC.

T-1000G Carbon Fiber
Safety Factor = 1.5
Internal Length/Diameter = 3

5,000 psia

7,500 psia

10,000 psia

15,000 psia

90 kWh

45 kWh

1 kWh

5 kWh

10 kWh

System Volume, liters (y-axis: 0, 50, 100, 150, 200, 250)

System Weight, kg (x-axis: 0, 5, 10, 15, 20, 25, 30, 35)

Advanced Pressurized Hydrogen Tankage System (Safety Factor = 1.5)

T-1000G Carbon Fiber
Safety Factor = 1.5
Internal Length/Diameter = 3

5,000 psia
7,500 psia
10,000 psia
15,000 psia

10 kWh
5 kWh
1 kWh

System Volume, liters

System Weight, kg

Advanced Pressurized Hydrogen Tankage System (Safety Factor = 2.25)

DIRECTED TECHNOLOGIES, INC.

T-1000G Carbon Fiber
Safety Factor = 2.25
Internal Length/Diameter = 3

**Advanced Pressurized Hydrogen
Tankage System
(Safety Factor = 2.25)**

DIRECTED
TECHNOLOGIES, INC.

System Volume, liters

T-1000G Carbon Fiber
Safety Factor = 2.25
Internal Length/Diameter = 3

5,000 psia

7,500 psia

10,000 psia

15,000 psia

10 kWh

5 kWh

1 kWh

System Weight, kg

Compressed Hydrogen Tankage System
Weight, Volume, and Dimensions

T-1000G Carbon Fiber
Safety Factor = 1.5

	1 kWh	10 kWh	90 kWh
5,000 psia System			
Total System Weight (kg)	1.39	4.22	26.96
Usable H2	0.05	0.53	4.74
Fiber	0.15	1.54	13.88
resin	0.07	0.75	6.71
liner	0.01	0.07	0.29
bosses	0.24	0.48	0.48
pressure reducer	0.50	0.50	0.50
Flow Metering Assembly	0.36	0.36	0.36
Internal Volume (liters)	2.31	23.03	207.27
External Volume (liters)	2.45	24.38	219.23
External Dimensions (cm)			
Total Length	30.85	66.37	138.05
Total Diameter	10.47	22.51	46.80

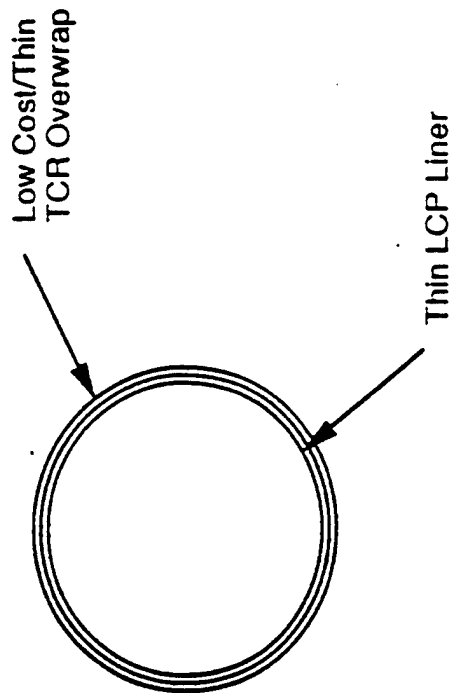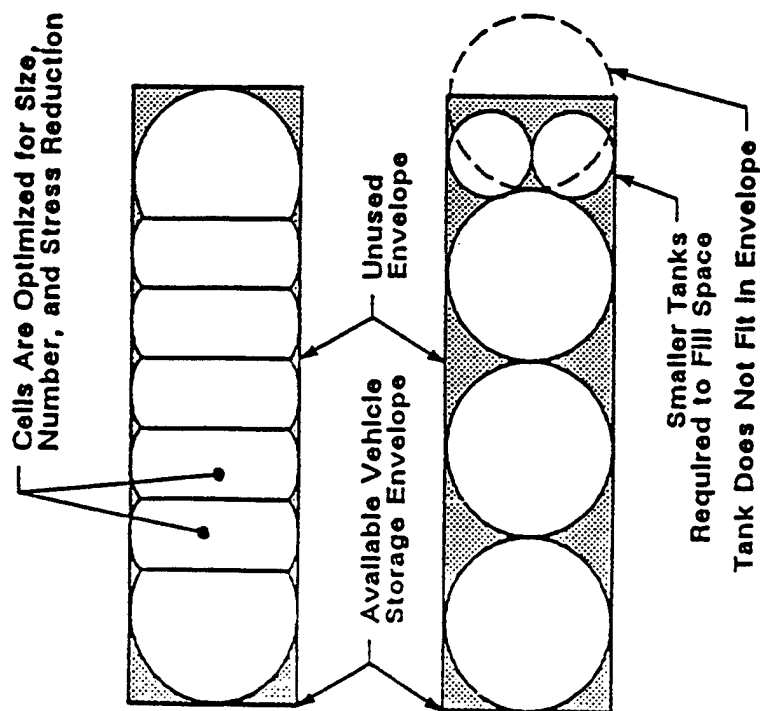|	1 kWh	10 kWh	90 kWh
10,000 psia System			
Total System Weight (kg)	1.44	4.65	30.75
Usable H2	0.05	0.53	4.74
Fiber	0.18	1.83	16.43
resin	0.09	0.88	7.95
liner	0.01	0.06	0.28
bosses	0.24	0.48	0.48
pressure reducer	0.50	0.50	0.50
Flow Metering Asbly	0.36	0.36	0.36
Internal Volume (liters)	1.37	13.66	122.74
External Volume (liters)	1.54	15.26	137.07
External Dimensions (cm)			
Total Length	26.12	56.19	116.86
Total Diameter	9.03	19.38	40.27

	1 kWh	10 kWh	90 kWh
15,000 psia System			
Total System Weight (kg)	1.48	5.05	34.36
H2	0.05	0.53	4.74
Fiber	0.21	2.10	18.90
resin	0.10	1.02	9.14
liner	0.01	0.05	0.23
bosses	0.24	0.48	0.48
pressure reducer	0.50	0.50	0.50
Flow Metering Asbly	0.36	0.36	0.36
Internal Volume (liters)	1.05	10.48	94.11
External Volume (liters)	1.24	12.35	110.83
External Dimensions (cm)			
Total Length	24.11	51.86	107.84
Total Diameter	8.46	18.17	37.74

Thiokol's Approach

▲ Fuel storage products that allow more fuel to be stored in the same space at lower cost

▲ Conformable Storage

▲ Thin Walled Cylinders

Low Cost/Thin
TCR Overwrap

Thin LCP Liner

Cells Are Optimized for Size, Number, and Stress Reduction

Unused Envelope

Available Vehicle Storage Envelope

Smaller Tanks Required to Fill Space

Tank Does Not Fit In Envelope

THIOKOL
SPACE · DEFENSE · FASTENING SYSTEMS

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**DIRECTED
TECHNOLOGIES, INC.**

1) Demonstration of full Metalized Bladder Liners

2) Appropriate Safety Factor (1.5 vs. 2.25)

3) Fast Fill Heating Rise

4) Safety
    - Burst
    - Shrapnel
    - Los Angeles MTA Incident

5) Light Weight High Pressure Pressure-Reducers
    and Solenoid Valves

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Energy Film: A Safe Portable Source of Hydrogen

Dr. Michael Monsler
Dr. Charles Hendricks
Mr. Thomas Walsh

Workshop on Hydrogen
Storage and Generation
Technologies

Orlando Florida
April 8-10, 1997

WJSA

W. J. Schafer Associates, Inc.

An Employee-Owned Small Business

Energy & Environment
Group

303 Lindbergh Avenue
Livermore, CA 94550
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(520) 447-0544/fax
mmonsler@wjsa.com

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An Introduction to W. J. Schafer Associates Inc.

- **WJSA provides technology advice to governments and industry in four key business areas**
  - Information Technology, Modeling and Simulation
  - Research and Technology Development
  - Energy and Environment
  - Defense and Space Systems

- **WJSA has six main offices in Boston, Washington DC, Huntsville, Albuquerque, Los Angeles and San Francisco, and 6 smaller satellite offices**

- **WJSA is an employee-owned small business with 200 employees and $31M in annual revenues.**
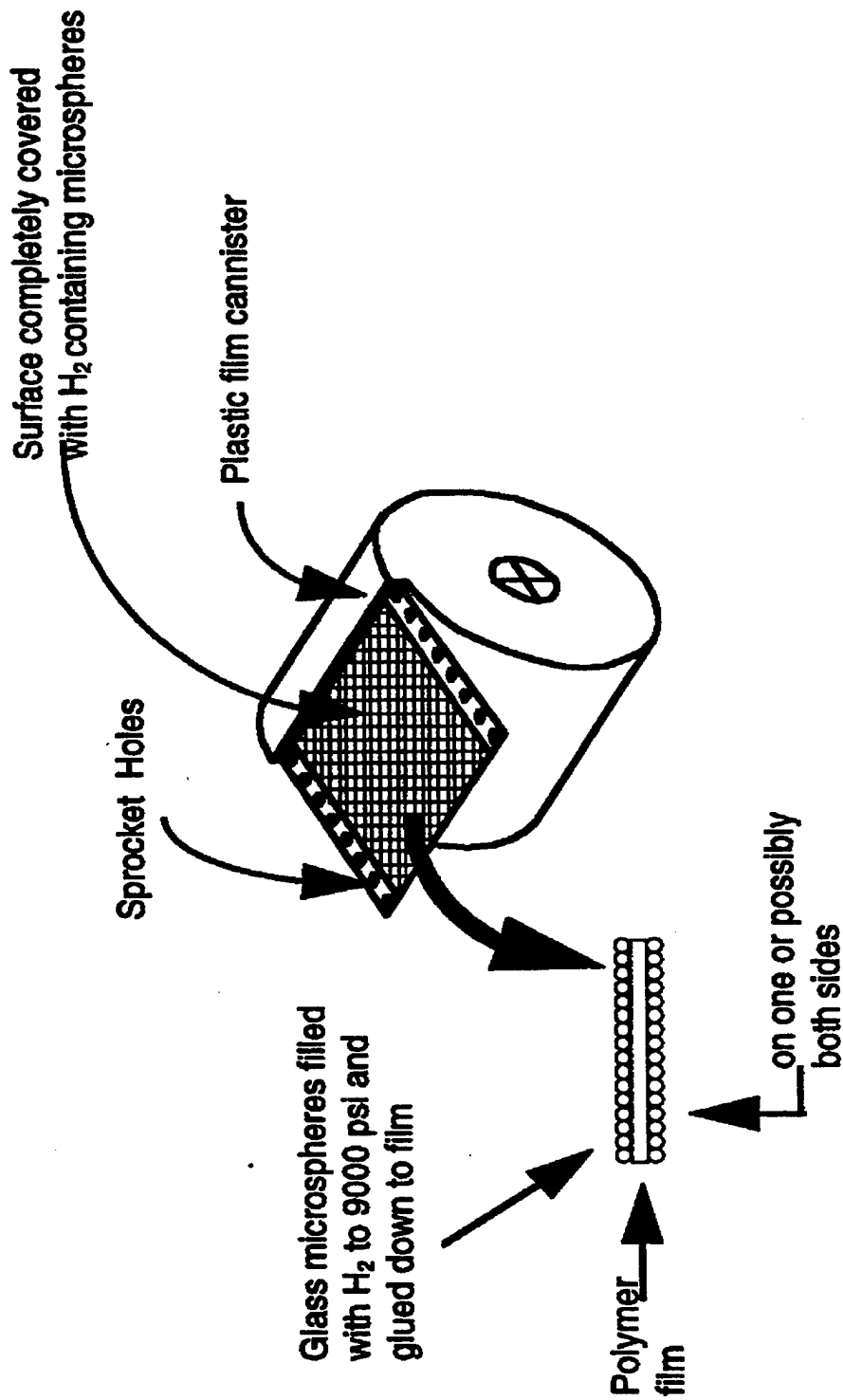
Energy Film: A Safe Portable Source of Hydrogen

SBIR OSD96-001

- Small PEM fuel cells (< 200 W) are becoming available to power battlefield electronics for the footsoldier

- They lack a safe convenient source of hydrogen. At present, compressed gas tanks are heavy and bulky to use and recycle

- The goal is to;

  - replace the standard ARMY BA 5590 battery, in missions where high power demand causes extremely short battery life

  - store 10-120 grams of H_2 and deliver it at up to 10 gms/hr in all military environments, safely and reliably

- The customer is the US Army CECOM, Ft. Belvoir VA

- Phase I contract is for $99K, 6 month duration.

- For a safe and convenient H_2 storage medium, WJSA proposed to use glass microspheres filled to 9000 psi and affixed to a polymer substrate in a uniform layer. Energy Film would be packaged and transported like photo film.

- Hydrogen would be released to the Fuel Cell in a controlled manner by pulling the Energy Film through rollers and crushing the microspheres at a known rate.

The Concept of Energy Film
for H_2 Storage and Transport

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Surface completely covered
with H_2 containing microspheres

Plastic film cannister

Sprocket Holes

Glass microspheres filled
with H_2 to 9000 psi and
glued down to film

Polymer
film

on one or possibly
both sides

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Storage of Hydrogen in Glass Microspheres

- **Hydrogen is stored at high pressure in a jillion (10^{11} per kg) small independent spherical cavities**
    - Pressure limits can be very high, perhaps 10,000 psi
    - Storage is passive, at room temperature, for long term

- **The hydrogen released is very pure - will not poison fuel cells**

- **The fuel tank or container for a bed of glass microspheres**
    - Can conform to any shape
    - Is at low pressure, and should be inexpensive

- **The hydrogen can be released by either...**
    - Heating the microspheres to 200-350 C, with less heat required than needed for an equivalent hydride bed
    - Or by crushing the microspheres to release all the stored H_2, when recycling is not needed

- **Glass microspheres have been used to store H_2 in Inertial Confinement Fusion (ICF) for over 20 years**
    - WJSA uses a droplet generator process to make microspheres of very uniform mass, high concentricity, and low defect density
    - Commercial shells used for insulation, fillers, etc. have too many defects to be good pressure vessels

The microspheres are very small, very thin wall glass shells

.5 - 1.5µm

25 - 200µm

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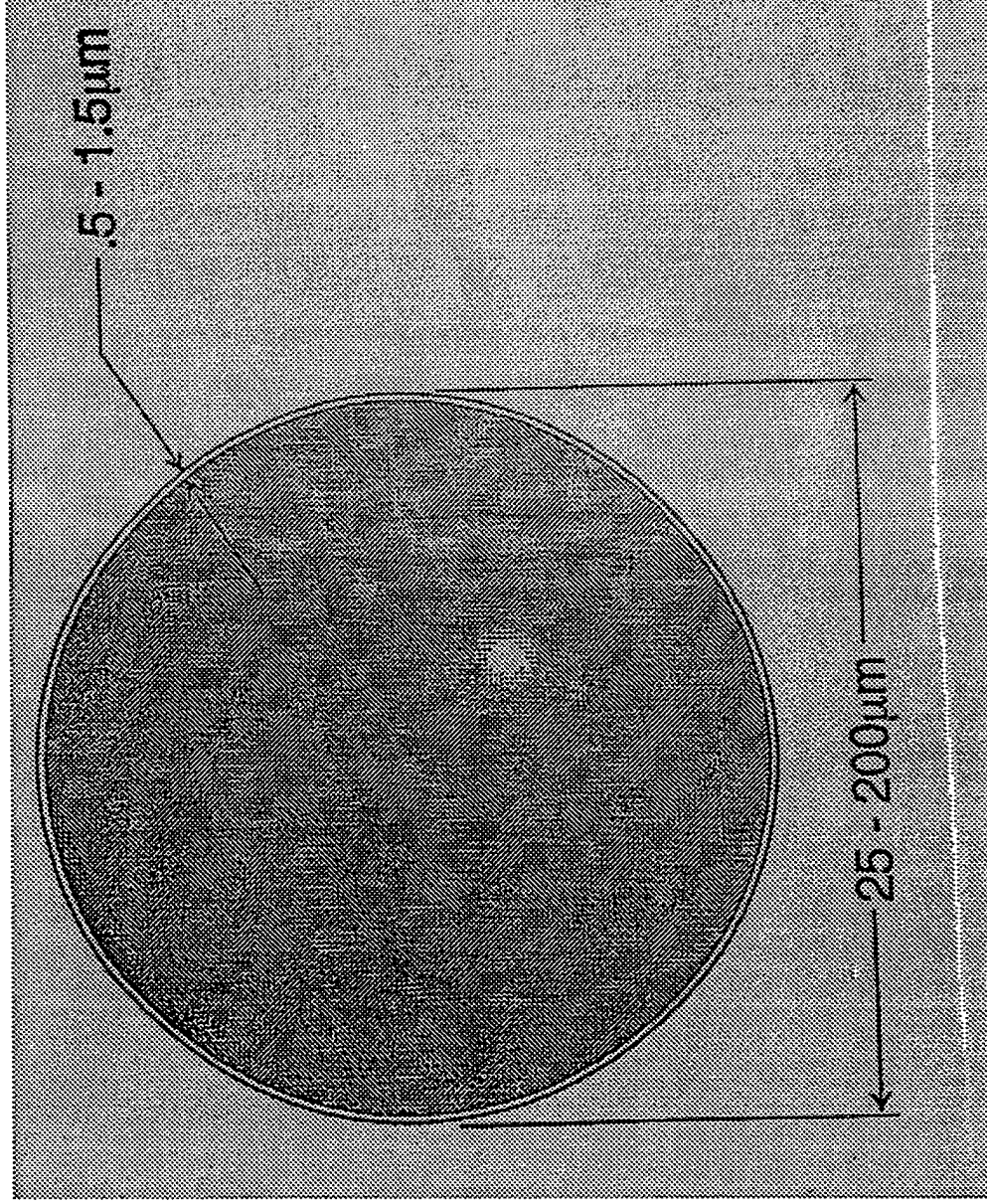
The strength of glass is the key physical property determining the energy storage capacity

- Failure strength of glass is very sensitive to the presence of microscopic surface cracks, and the method of processing, but not a strong function of composition
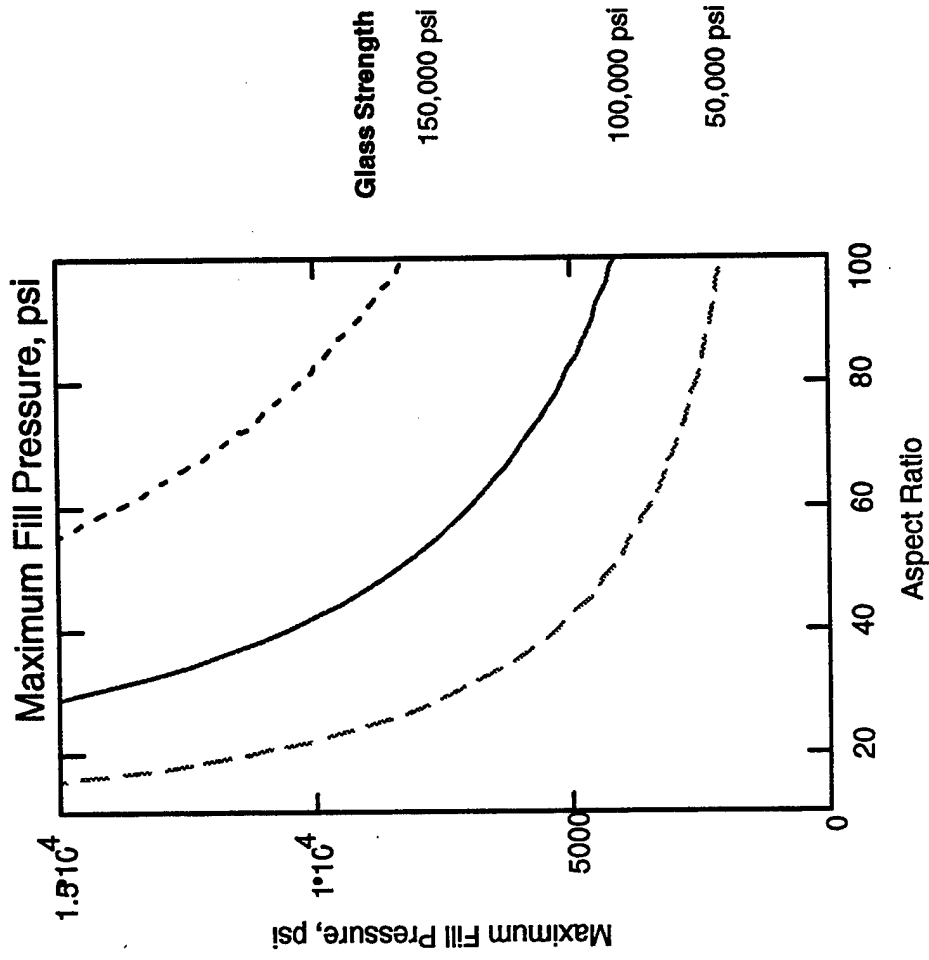
	MPa	kpsi
Theoretical glass strength:		
From theory of brittle solids(1):	~ 35,000	~ 5000
Typical measured glass strength values(2):		
Ordinary glass products (bottles, etc.)	14 - 70	2 - 10
Freshly drawn glass rod	70 - 140	10 - 20
Abraded glass rod	14 - 35	2 - 5
Wet, scored glass rod	3 - 7	0.4 - 1
Armored glass	350 - 500	50 - 73
Freshly drawn glass fibers	700 - 2100	100 - 300
Experimentally achieved glass strength values:	~ 7000	~ 1000
Commercial glass microspheres fail at	~ 350	~ 50
Glass microspheres made at LLNL failed at	~ 1000	~ 145
Glass microspheres.(3) failed at	800 - 1600	120 - 240

References:
1. E. Orowan, Z. Krist, A89, 327-343 (1934)
2. A.K. Varshneya, *Fundamentals of Inorganic Glasses*, Academic Press, Inc. (1994)
3. J. Milewski, LANL, 1978, unpublished

Thinner shells have more volume available for hydrogen, but they hold far less pressure

Maximum Fill Pressure, psi

Glass Strength

150,000 psi

100,000 psi

50,000 psi

Aspect Ratio

Fraction of Volume Available for H2

Sphere

Bed
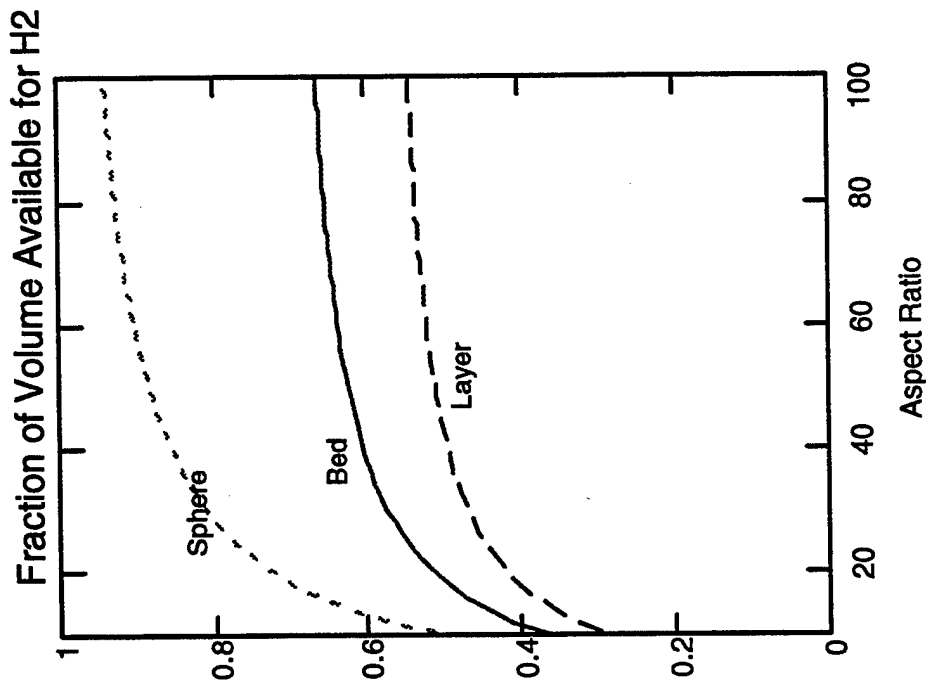
Layer

Aspect Ratio

Aspect ratio = diameter / thickness

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Packing Fractions of both a Volumetric Bed and a Planar Layer of Microspheres

Max. theoretical volumetric packing fraction for a close-packed bed of spheres

$$pf_{bed} := \frac{\pi}{3 \cdot \sqrt{2}} \qquad pf_{bed} = 0.74$$

Max. theoretical volumetric packing fraction of a single planar close-packed layer of spheres

$$pf_{layer} := \frac{\pi}{3 \cdot \sqrt{3}} \qquad pf_{layer} = 0.605$$

Fraction of volume of a single microsphere available for H2

$$fH2(ar) := \left(1 - \frac{2}{ar}\right)^3 \qquad fH2(ar1) = 0.857$$

Fraction of a single microsphere that is glass

$$fgl(ar) := 1 - fH2(ar) \qquad fgl(ar1) = 0.143$$

Derating of the theoretical packing fraction

$$\eta_{pf} := 0.95$$

Fraction of bed volume available for H2

$$fbv(ar) := \eta_{pf} \cdot pf_{bed} \cdot fH2(ar) \qquad fbv(ar1) = 0.603$$

Fraction of planar layer volume available for H2

$$fpl(ar) := \eta_{pf} \cdot pf_{layer} \cdot fH2(ar) \qquad fpl(ar1) = 0.492$$

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To calculate the properties of EF, assume a thin mylar substrate with two layers of GMS and adhesive

For the calculation, these two cases are equivalent
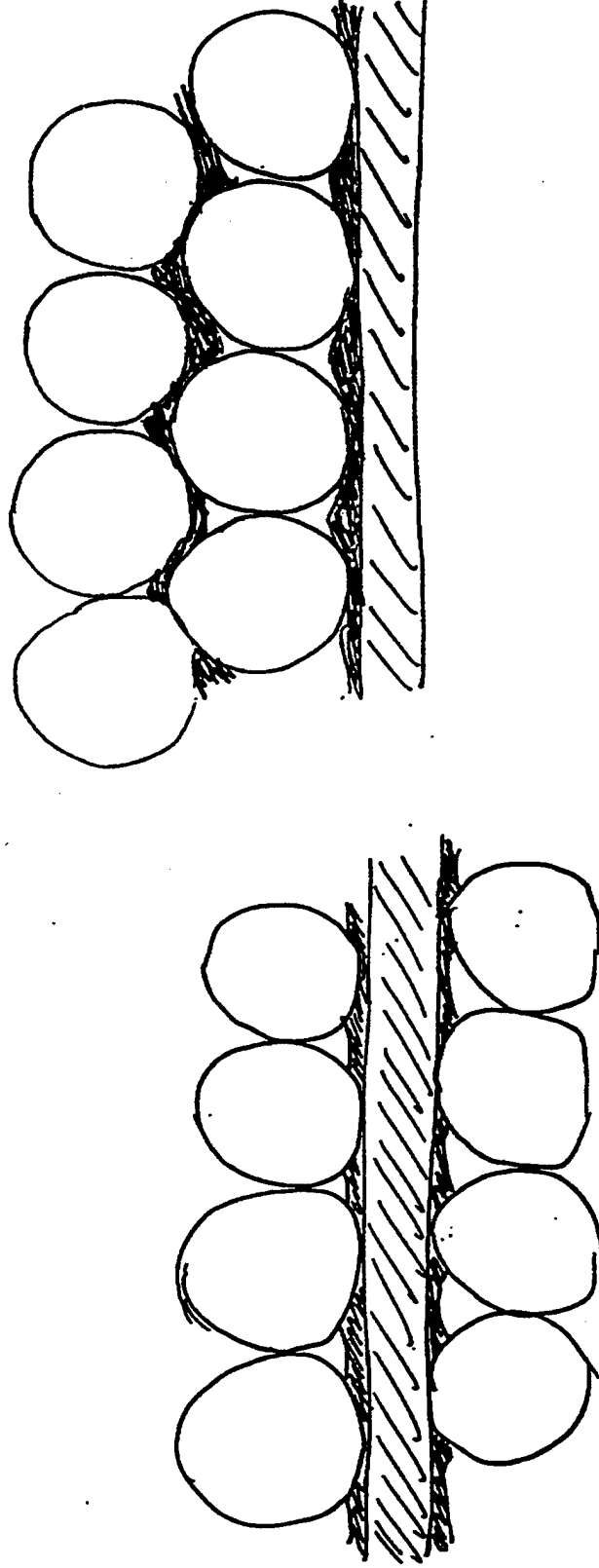
Substrate   10 microns thick
Adhesive   3 microns thick
Shell diameter 100 microns

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The volumetric energy density of Energy Film improves with shell aspect ratio and diameter

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Vol. Energy Density of EF

Assumes p = 9000 psi and diameter = 100 microns

Aspect Ratio

Vol. Energy density, MJ/liter

Energy Film

Assumes p= 9000 psi and aspect ratio = 40

Shell Diameter

Vol. Energy Density, MJ/liter

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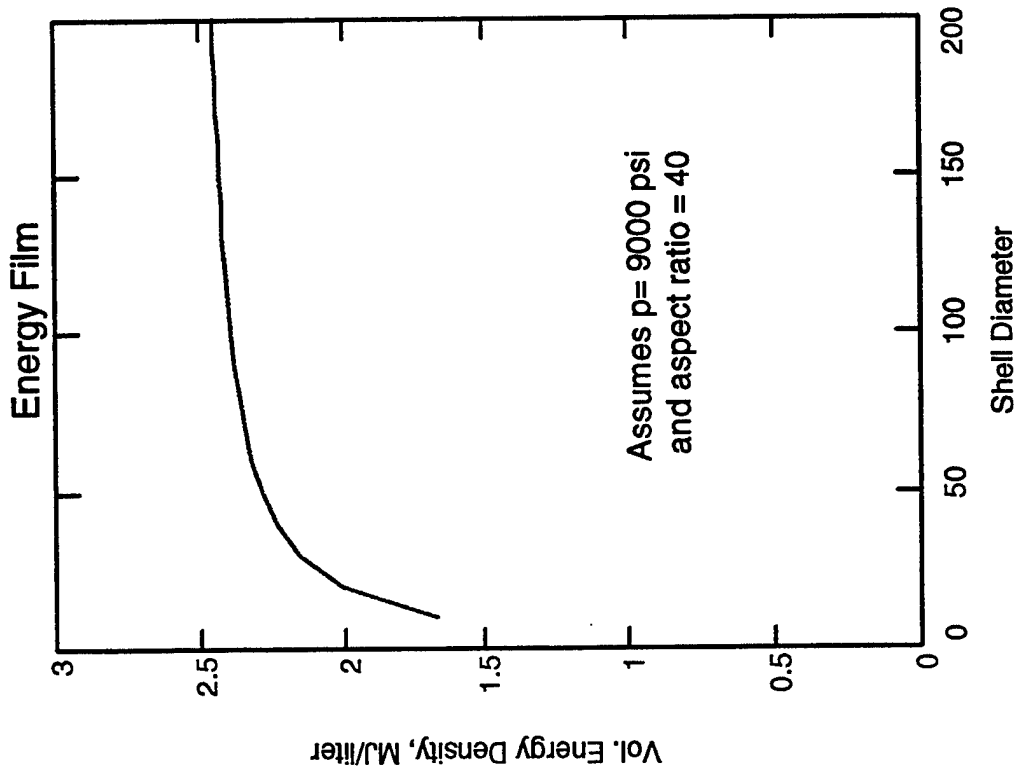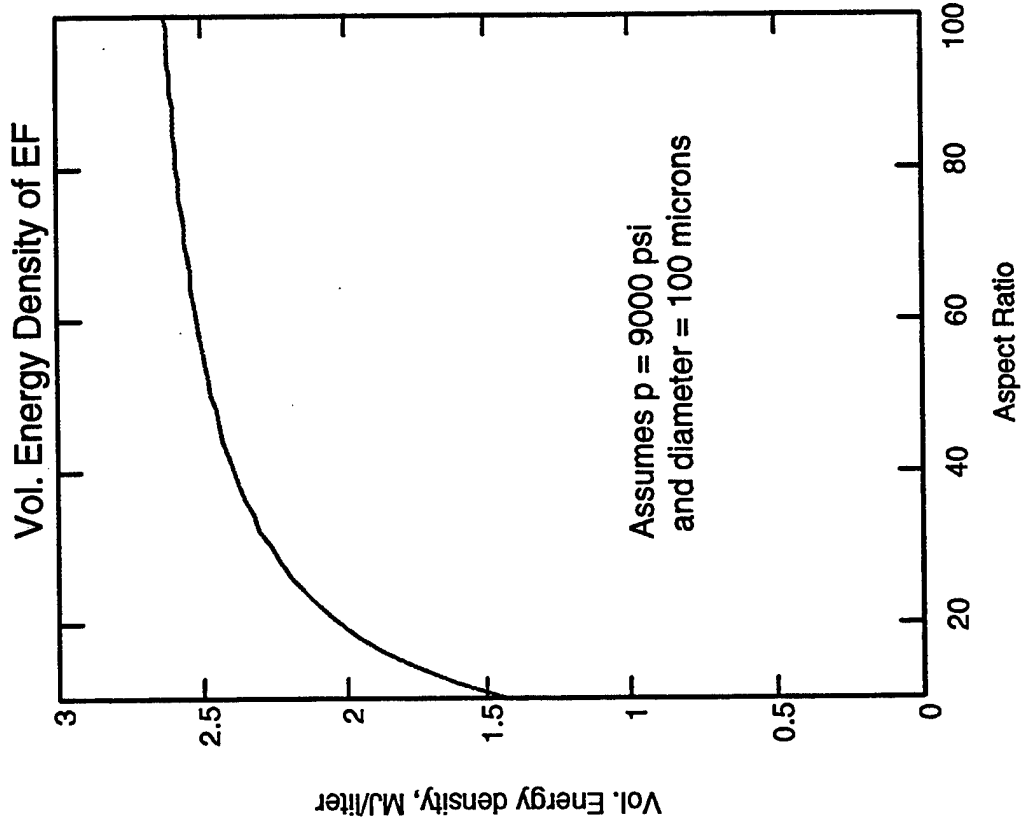
The H$_2$ mass fraction of Energy Film increases with shell diameter, and has a broad maximum with respect to aspect ratio

Fraction of Pure H2 by Weight

Diameter
d = 300 microns

d = 200 microns

d = 100 microns
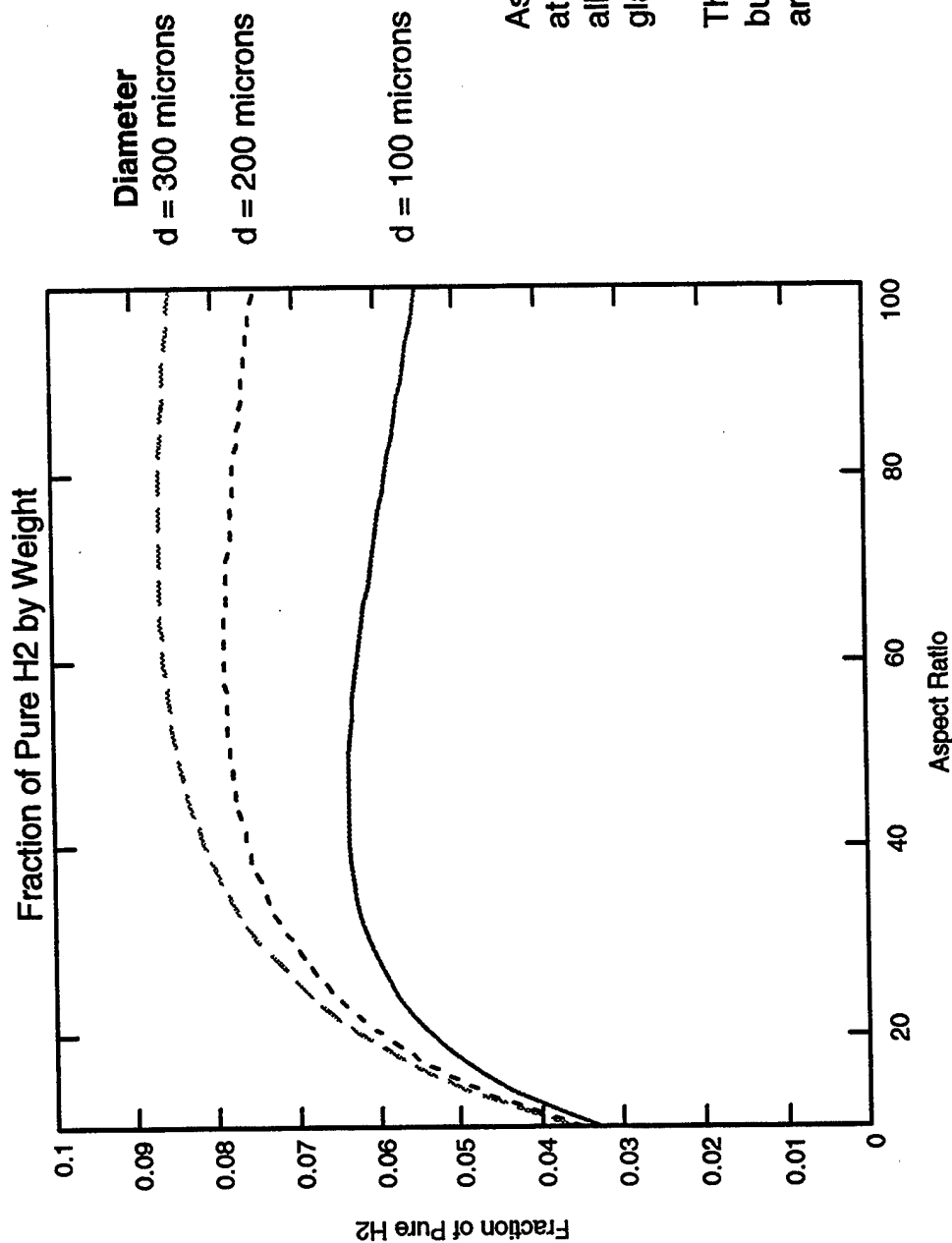
Assumes we operate at the highest fill pressure allowed by the strength of glass for each aspect ratio.

Thinner shells weigh less, but hold less pressure, and therefore less energy.

Fraction of Pure H2

Aspect Ratio

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The H2 mass fraction of Energy Film (for a fixed pressure), increases with aspect ratio until a limit determined by the strength of glass

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Diameter
d = 300 microns

d = 200 microns

d = 100 microns

In this case the pressure is held fixed at p = 9000 psi, and the aspect ratio is limited to 46 by the strength of glass.

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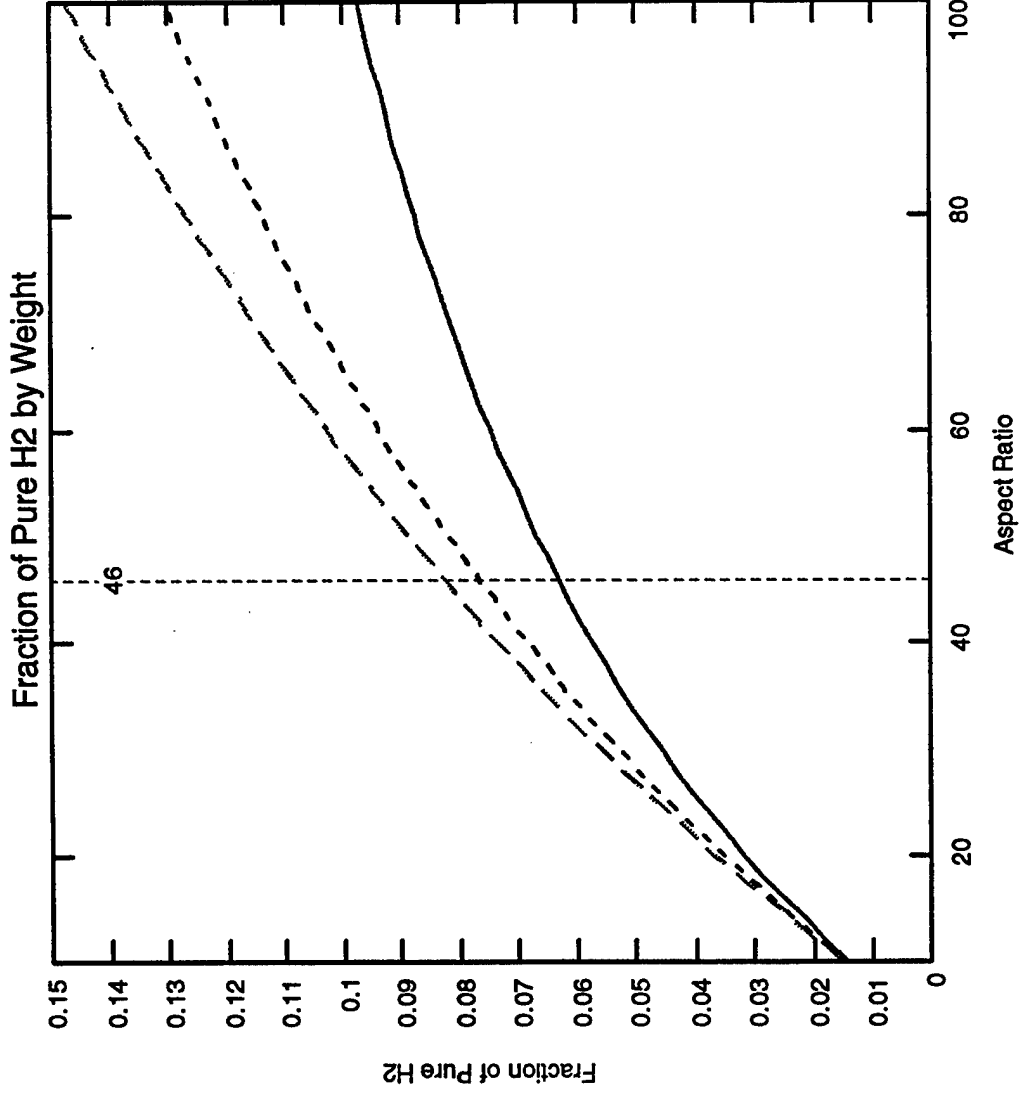
Example: Design a cartridge of Energy Film for a particular mission

Electrical power to be generated in PEM FuelCell	P_e = 150 watts
Fuel Cell efficiency	50 %
Discharge time @ full power	T = 4 hours
Electrical energy stored	E_e = 600 watt-hr = 2.16 MJ
Mass of stored Hydrogen	M = 30.47 gm
Conversion rate, H_2 to electricity	19.7 watt-hr/(gm H_2)
Hydrogen usage rate needed	7.62 gm/hr
Glass microspheres Diameter	d = 100 microns
Aspect ratio	ar = 40
Fill pressure	p = 9000 psi
Energy Film parameters	Substrate thick. = 10 microns
(Mylar with 2 layers of microspheres)	Total thickness = 210 microns
Width of film (no sprocket holes)	Width = 10 cm = 4 in.
Film pull-rate required	v = 0.6 cm/sec
Length of film required	Length = 86 m
Size of a roll of Energy Film	Height = 10 cm = 4 in.
	Diameter = 15.2 cm = 6 in.
Weight of the roll only	Mass = 532 gm = 1.17 lb
Weight inc. plastic spool and container (60 gm)	Mass = 592 gm = 1.3 lb
Fraction of hydrogen by weight	5.1 % H_2

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Some lessons-learned in making the coated substrate for Energy Film

- We have performed experiments on several combinations of tapes and adhesives - and found many combinations that don't work

- Box tape (with preapplied uniform adhesive layer) looked promising in early experiments
    - But adhesive migrates over top of shells, stays sticky
    - Need an adhesive that sets, yet stays flexible

- Diluted Contact Cement works OK
    - Difficult to make a uniform application of thin layer
    - If too thick, get heavy clumping of shells
    - We will try a flexible UV setting epoxy next

- Can't use a roller to press down shells onto adhesive - get excessive breakage

- Photo film stock is not usable - will lead to low energy density
    - It is unnecessarily thick (~ 140 microns)
    - Sprocket holes seem unnecessary (unutilized surface area)
    - Go to Mylar or Kapton (10-20 microns)

- A double-sided coating of microspheres is unlikely to work
    - Microspheres break from rubbing and rolling of film
    - But more than one layer on a single side of film seems feasible

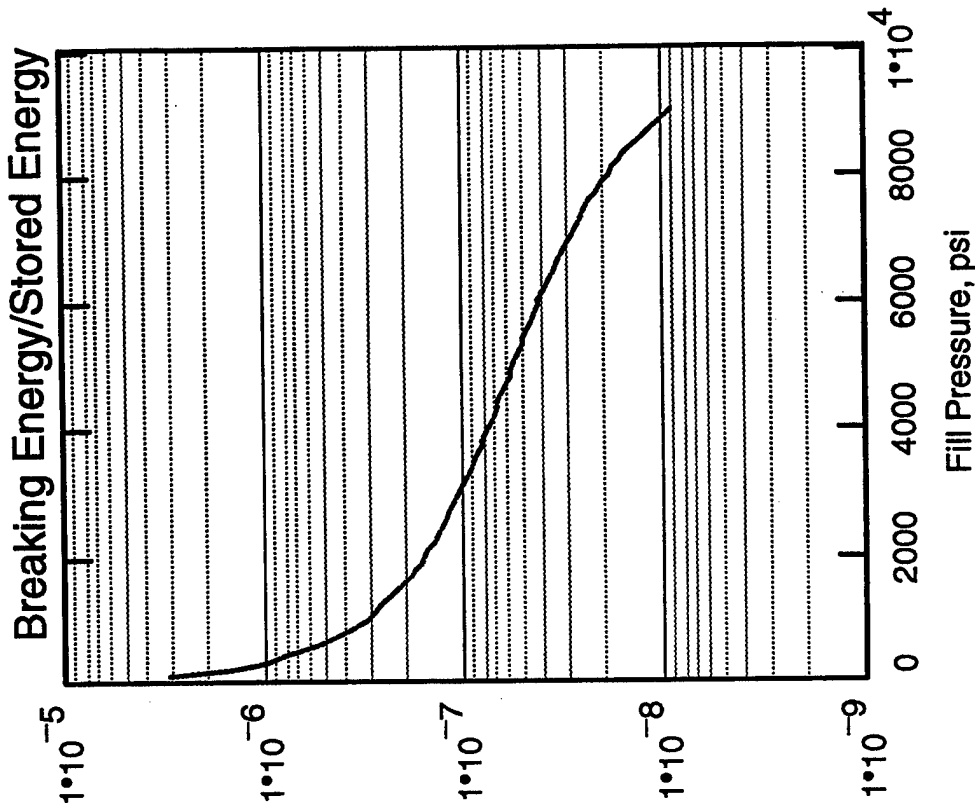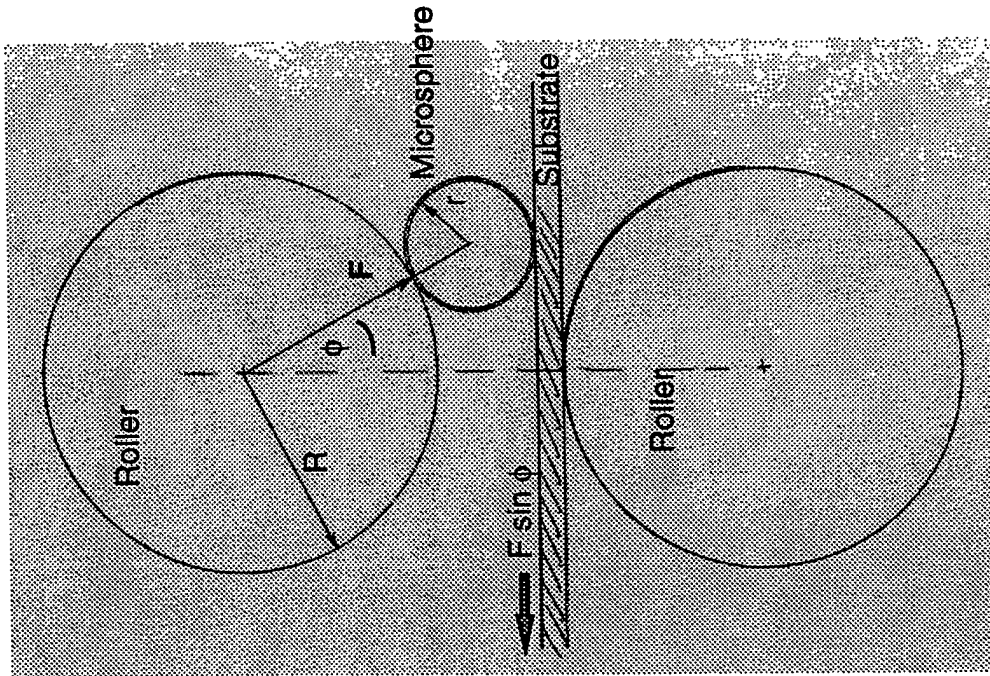# We have successfully filled shells at ~ 2000 psi and released the hydrogen by crushing

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- We constructed a high-pressure hydrogen filling apparatus to fill shells at elevated temperature (~ 350 C)

- We have experimented with our own shells and with 3M Scotchlite™ Glass Bubbles (30-100 micron diameter, ~ 1 micron wall)

- Using commercial bottled hydrogen limited to 2200-2400 psi, we filled several CCs of glass microspheres by stepping up the pressure slowly, such that each pressure increment stays below the buckling limit of thin shells.

- After a few trials in which we crushed the majority of shells by filling too fast, we are now getting nearly a 100% yield in the filling process

- We confirmed the storage and release of hydrogen by breaking an individual glass shell under water and measuring the bubble volume

- When brought back down to room temperature, the shells contain H_2 at about 1100 psi

- We have added a small high-pressure generator capable of reaching much higher fill pressures (12,000 psi), but have not used it yet.

The power required to pull the energy film through the crushing rollers is negligible compared to the hydrogen energy release rate

- We measured the force needed to pull the Energy Film (2.5 cm wide) through the rollers at approximately 1 cm/sec.

- 90-110 grams force was required. For our nominal 10 cm wide Energy Film, this translates to...

  - An energy required to overcome friction and break the shells of

    - E_{pull} = 3.92 joules/meter of film

  - A nominal heating value of energy stored in Energy Film (@ 9000 psi) of

    - E_{store} = 25,077 joules/meter of film

  - If we were to use electricity generated in the fuel cell (50% effic.) to run a DC motor (60% effic.) to pull the film, the recirculated power fraction would be
    $f = (E_{pull}/0.60)/(E_{store} *0.50) = 5.2 \times 10^{-4}$

- Because the pulling force did not vary much with film substrate and the roller-bearing friction is trivial, we believe that the dominant energy loss mechanism is the shell-crushing process

- Since the pulling-power requirement is so small, rather than recirculate electricity generated by the fuel cell to run a motor, we may use a simple clock spring to pull the film

- The clock spring would be wound or cocked automatically in the film loading process - so the fuel cell efficiency would not be affected.

Calculations confirm that the energy required to crush a shell is comparatively small, and that filled shells are easier to break since they are already near the stress limit

Breaking Energy/Stored Energy

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The H_2 generator would be part of the fuel cell apparatus, not part of the energy film cartridge

- Conceptually, the H_2 generator may look like a camera body. It would be an integral part of the fuel cell hardware.

- The roll of Energy Film is loaded into the H_2 generator like loading a camera. Inexpensive lightweight commercial analogies of this mechanism exist.

- Loading the Energy Film cocks a clock spring which drives the pulling spool.

- The H_2 generator pulls the Energy Film through the rollers, liberating H_2 at the desired rate.

- In Phase II, we will design, build and demonstrate a prototype of the H_2 generator, coupled to a FC.

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This is the experimental H₂ generator

- It is a steel vacuum chamber in which the film can be pulled through crushing rollers at a measured rate

- A Residual Gas Analyser (RGA) will be attached to measure the amount of H_2 liberated per length of energy film
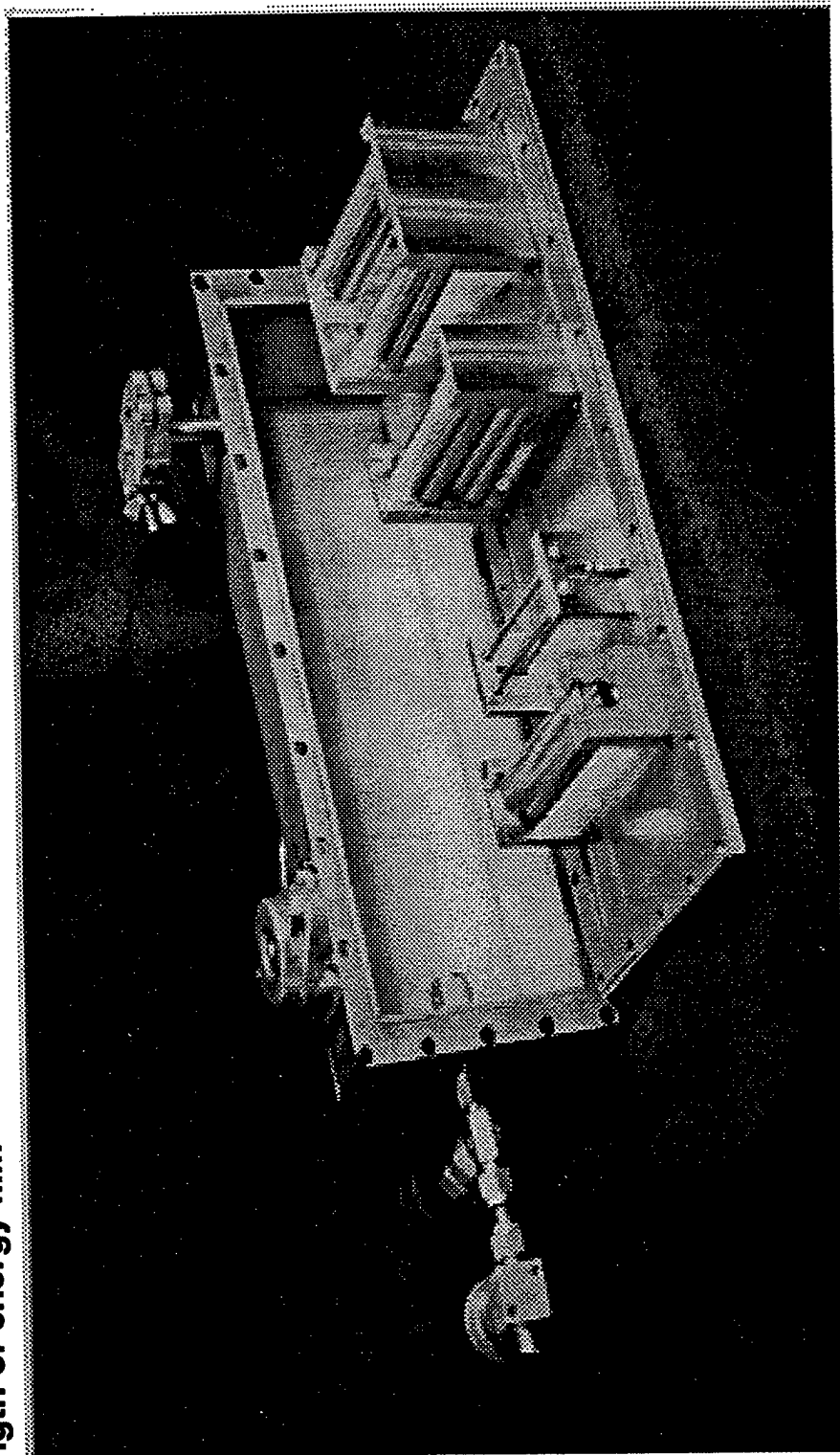
The vacuum system is ready for the installation of the experimental H_2 generator and the RGA

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- The experimental H_2 generator will be attached to this vacuum pumping station

- The Residual Gas Analyser (RGA) will also be attached to this vacuum system

- The amount of hydrogen gas liberated will be measured as a function of length of film pulled through the crushing rollers

- We will also measure the amount of CO, CO_2, H_2O and other contaminants which may evolve

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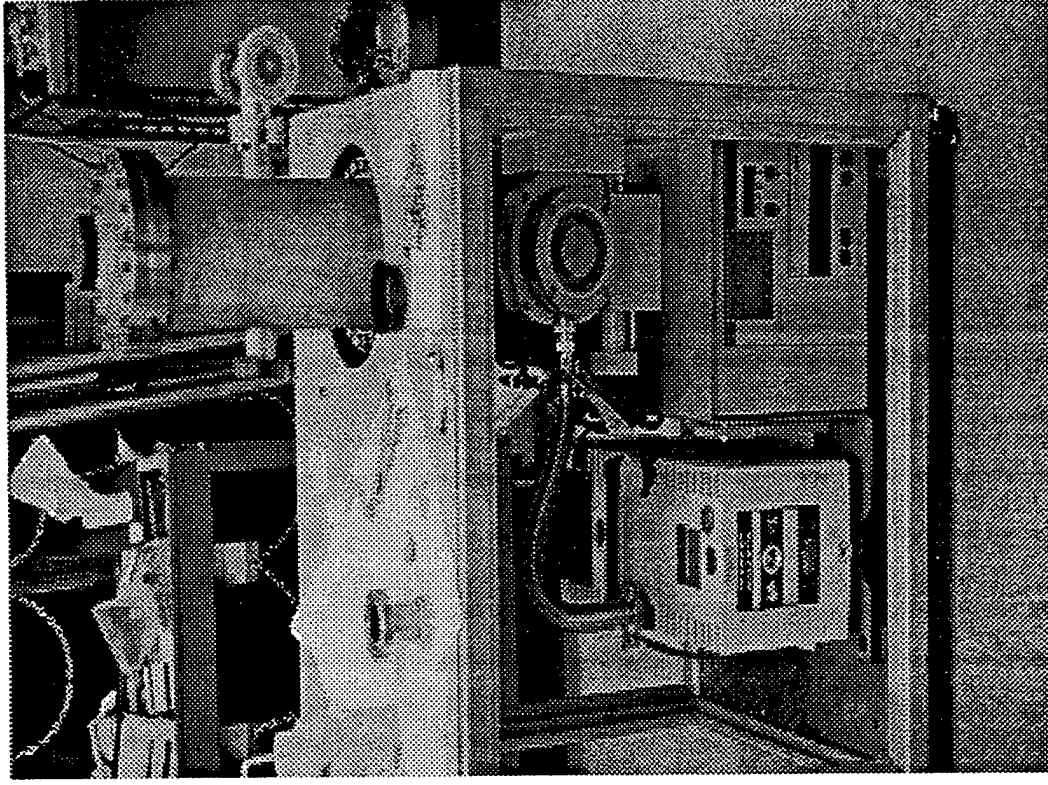
Energy Film may have some distinct advantages over the alternatives for the U.S. Army

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- **A HUGE # of SMALL INDEPENDENT CONTAINERS offers GREATER SAFETY** - WJSA believes that a bullet penetrating a Energy Film Cartridge will liberate the H_2 of only the struck microspheres, unlike a gas cylinder which would empty completely and immediately

- **REDUCED WEIGHT** - WJSA believes that there is a tremendous logistic advantage in not having to carry empty gas cylinders or hydride beds back from the field for recharging

- **GREATER CONVENIENCE** - WJSA believes that because Energy Film is non-hazardous and can be made disposible (just sand and biodegradable plastic), it would be preferred in the field.

- **REDUCED COST** - WJSA does not know how much Energy Film will cost in mass production, but imagine the limit...potentially as low as Saran Wrap and sand. (H_2 compression costs will dominate)

Are a soldier's razor blades taken back for resharpening?

How about their food and drink packages?

Why recycle and recharge heavy energy packages?

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Objectives of Phase II SBIR

- Perfect process for mass-producing uniform glass shells in quantity

- Demonstrate filling and handling of shells up to 10,000 psi

- Team with a firm like 3M or Polaroid with commercial experience in coatings and polymer films – a manufacturing partner

- Make 100s of meters of energy film with much thinner substrate and adhesive thicknesses – optimize energy storage density

- Demonstrate a 'clockspring' driven or a low-power electrical film-puller

- Design and construct a fully functional H_2 Generator prototype that seals tight, can be easily loaded and unloaded, generates a given hydrogen flowrate

- Demonstrate a complete 600 watt-hour system, with an H_2 Generator integrated with a 150 watt PEM fuel cell provided by the Army

- Operate system reliably for hours at a time

- Assess cost, safety, efficiency and utility of integrated Energy Film concept in field operation

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Chemical Hydrides

Solid State Hydrogen Gas Generation System

by

Ottmar H. Dengel

and

Werner F. Beckert

Royal Systems

for

Workshop on Storage and Generation of Hydrogen

8 - 10 April 1997
Orlando Florida

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Topics of Presentation:

- Hydrogen Gas Generating Composition

- Requirements for a Hydrogen Gas Generator System

- Hydrogen Gas Generator Design

- System Weight Considerations

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TABLE I
Properties of Hydrogen Generating Compositions

	H$_2$ - Generating Formulation	H$_2$ yield per reactant weight	Stability	Comments
1	NH$_4$B$_4$H$_4$	20.7%	dec. -40^0 C	unstable
2	NH$_3$BH$_3$	19.6%	dec. ~100°C/50^{0}C	Mix: fine solids, high burn.rate, high T
3	BH$_2$(NH$_3$)$_2$BH$_4$	19.6%	dec. <95°C	Mix: fine solids, high burn rate , high T,
4	NH$_3$B$_3$H$_7$	17.8%	dec. 74°C	unstable
5	N$_2$H$_4$ x 2BH$_3$	16..9%	dec. ~100°C	Mix: fine solids, high burn rate, el.stat.
6	Mg(BH$_4$)$_2$ x 2NH$_3$	16.0%	dec. ~100°C	Mix: fine solids, high burn rate, high T,CO/NH$_3$
7	Li + H$_2$O	4.0%	not stable	not pursued
8	LiH + H$_2$O	8.0%	not stable	not persued
9	LiBH$_4$ + H$_2$O	10.5%	not stable	not pursued
10	NH$_4$F + LiBH$_4$	13.5%	dec. ~40^{0}c	unstable (DSC)
11	NH$_4$F + NaBH$_4$	10.7%	dec. ~45^{0}C	unstable (DSC)
12	NH$_4$F + LiAlH$_4$	10.7%	dec. 76^{0}C	unstable (DSC)
13	N$_2$H$_6$Cl$_2$ + LiBH$_4$	9.4%		no react. up to 400^{0}C (DSC)
14	NH$_4$Cl + LiBH$_4$	10.6%	dec. 60^{0}C	unstable
15	NH$_4$F + NaAlH$_4$	8.7%	dec. 107^{0}C	not pursued - NH$_4$F toxicity
16	Li$_3$AlH$_6$ + NH$_4$F	11.0%		compound not available
17	Li$_3$AlH$_6$ + NH$_4$Cl	9.0%		compound not available
18	N$_2$H$_4$ x 2BH$_3$ | LiAlH$_4$	13.0%		compound not available
19	N$_2$H$_4$ x 2BH$_3$ | MgH$_2$	13.9%		compound not available
20	N$_2$H$_4$ x 2BH$_3$ | NH$_4$Cl + 3LiAlH$_4$	10.3%		compound not available
21	NH$_4$Cl + 2LiAlH$_4$	8.5%	dec. ~100°C	onset of dec at 75 °C
22	NH$_4$Cl + NaAlH$_4$	7.4%	dec. ~170°C	very stable
23	NH$_4$Cl + 3LiAlH$_4$	8.4%	unknown	being evaluated
24	NH$_4$Cl + 1.2LiAlH$_4$	7.3%	unknown	being evaluated
25	NH$_4$Cl + NaAlH$_4$ + 2LiAlH$_4$	7.6%	unknown	being evaluated

Figure 1
Hydrogen Yield vs. Thermal Stability

1. NH_4BH_4 (pure cpd)
2. $NH_4B_3H_8$ (pure cpd)
3. NH_3BH_3 (pure cpd)
4. $BH_2(NH_3)_2BH_4$ (pure cpd)

5. $NH_3B_3H_7$ (pure cpd)
6. $N_2H_4 \cdot 2BH_3$ (pure cpd)
7. $Mg(BH_4) \cdot 2NH_3$ (in formulation)
8. $LiBH_4 + NH_4F$ (in formulation)

9. $LiAlH_4 + NH_4F$ (in formulation)
10. $NaAlH_4 + NH_4Cl$ (in formulation)
11. $2LiAlH_4 + NH_4Cl$ (in formulation)

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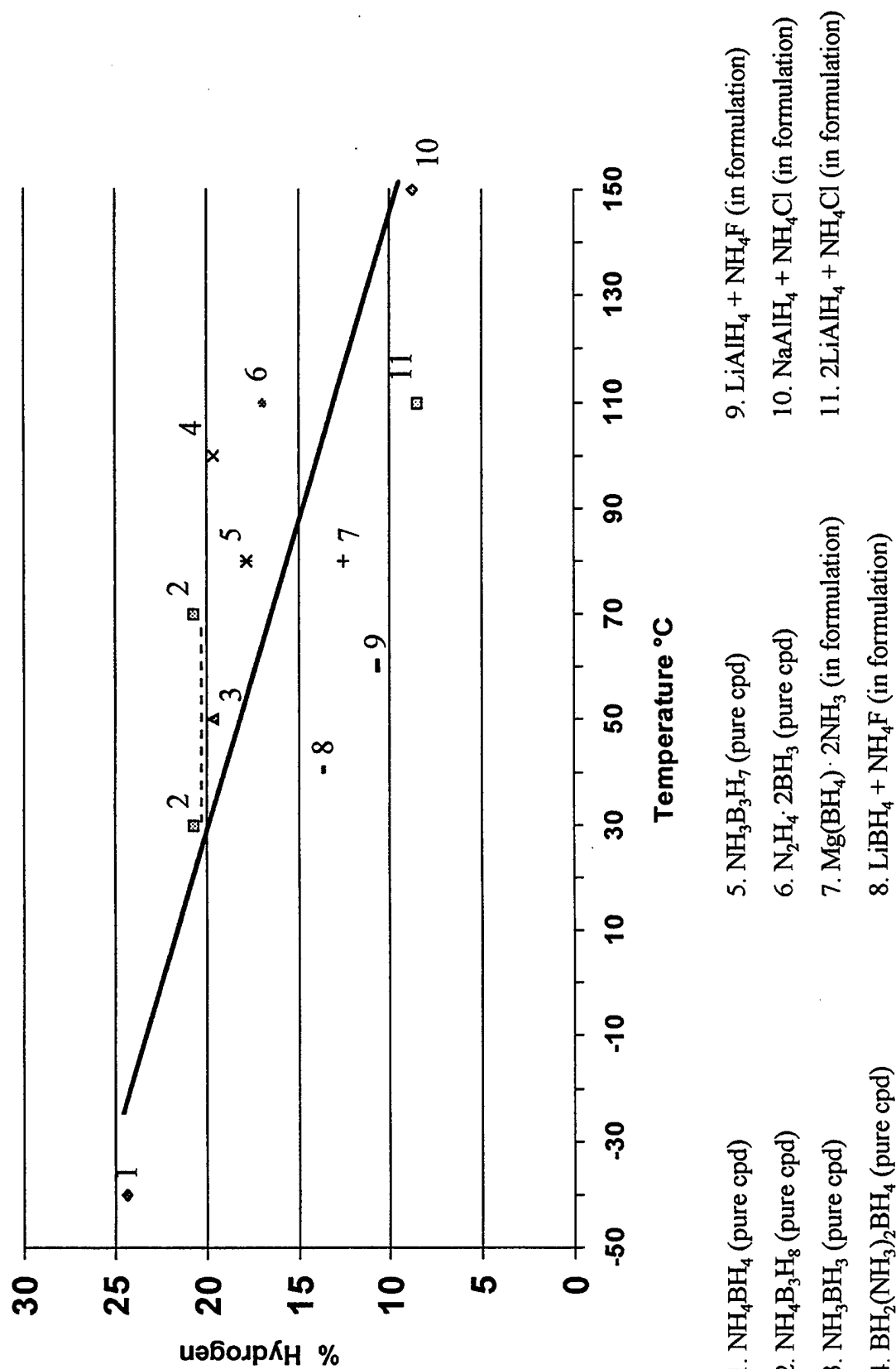
TABLE III

Calculated Values for Formulations Under Consideration

Reaction Equation	ΔH Kcal	ΔH/mole H₂	Theor. density before/after	Theor. Yield L/g	Theor. Yield g/100g
$NH_4F + LiBH_4 \rightarrow LiF + BN + 4H_2$	-48.2	-12.1	1.17/2.43	1.52	13.6
$NH_4F + NaBH_4 \rightarrow NaF + BN + 4H_2$	-40.3	-10.1	1.04/2.44	1.20	10.7
$NH_4F + LiAlH_4 \rightarrow LiF + AlN + 4H_2$	-85.7	-21.4	0.96/3.47	1.19	10.7
$NH_4F + NaAlH_4 \rightarrow NaF + AlN + 4H_2$	-74.1	-18.5	1.14/2.86	0.98	8.8
$NH_4F + 4LiH \rightarrow LiF + Li_3N + 4H_2$	+5.4	+1.4	0.91/2.23	1.30	11.6
$NH_4Cl + LiBH_4 \rightarrow LiCl + BN + 4H_2$	-36.9	-9.2	1.12/2.13	1.19	10.6
$NH_4Cl + NaBH_4 \rightarrow NaCl + BN + 4H_2$	-38.2	-9.6	1.30/2.20	0.98	8.8
$NH_4Cl + LiAlH_4 \rightarrow LiCl + AlN + 4H_2$	-74.4	-18.6	1.20/2.52	0.98	8.8
$NH_4Cl + NaAlH_4 \rightarrow NaCl + AlN + 4H_2$	-72.0	-18.0	1.37/2.52	0.83	7.4
$NH_4Cl + 4LiH \rightarrow LiCl + Li_3N + 4H_2$	+16.7	+4.2	1.16/2.04	1.05	9.4
$N_2H_6Cl_2 + 2LiBH_4 \rightarrow 2LiCl + 2BN + 7H_2$	-130.2	-18.6	1.08/2.13	1.06	9.4
$N_2H_6Cl_2 + 2NaBH_4 \rightarrow 2NaCl + 2BN + 7H_2$	-137.4	-19.6	1.25/2.19	0.87	7.5
$N_2H_6Cl_2 + 2LiAlH_4 \rightarrow 2LiCl + 2AlN + 7H_2$	-209.2	-29.9	1.16/2.52	0.87	7.7
$N_2H_6Cl_2 + 2NaAlH_4 \rightarrow 2NaCl + 2AlN + 7H_2$	-189.5	-27.1	1.32/2.52	0.74	6.6
$N_2H_6Cl_2 + 8LiH \rightarrow 2LiCl + 2Li_3N + 7H_2$	-26.9	-3.8	1.11/2.04	0.93	8.3
$NH_4Cl + 2LiAlH_4 \rightarrow LiCl + AlN + LiH + Al + 5.5H_2$	-71.9	-13.1	1.09/2.02	0.95	8.5
$NH_4Cl + 3LiAlH_4 \rightarrow LiCl + AlN + 2LiH + 2Al + 7H_2$	-69.4	-9.9	1.05/2.11	0.94	8.4
$NH_4Cl + 4LiAlH_4 \rightarrow LiCl + AlN + 3LiH + 3Al + 8.5H_2$	-66.9	-7.9	1.03/2.23	0.93	8.3
$NH_4Cl + NaAlH_4 + LiAlH_4 \rightarrow NaCl + LiH + AlN + Al + 5.5H_2$	-69.5	-12.6	1.21/2.18	0.85	7.6
$NH_4Cl + NaAlH_4 + 2LiAlH_4 \rightarrow NaCl + 2LiH + AlN + 2Al + 7H_2$	-67.1	-9.6	1.14/1.96	0.86	7.6
$NH_4Cl + NaAlH_4 + 3LiAlH_4 \rightarrow NaCl + 3LiH + AlN + 3Al + 8.5H_2$	-64.6	-7.6	1.1/1.8	0.86	7.7
$NH_4Cl + 1.2NaAlH_4 \rightarrow NaCl + AlN +0.2NaH + 0.2Al + 4.3H_2$	-69.4	-16.1	1.34/2.49	0.81	7.3

Hydrogen Gas-Generating Composition

$$1NH_4Cl + 3LiAlH_4$$
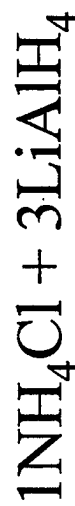
Reaction Chamber (number mols per 100g)

4.18259 H2	1.19626 Al&	1.19626 LiH&	0.59705 AlN&
0.59705 LiCl&	0.00000 Li2Cl2	0.00000 LiCl	0.00000 Li3Cl3
3.47E-08 LiH	1.55E-08 Li	2.34E-11 H	7.93E-12 AlH
2.212E-12 AlCl	7.26E-13 HCl	4.61E-13 Li2	9.55E-15 Al
3.26E-15 NH3			

Exhaust Gas (number mols per 100g)

4.18259 H2	1.19626 Al&	1.19626 LiH&	0.59705 LiCl&
5.97E-01 AlN&			

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Hydrogen Gas-Generator Predicted Features

Composition	Exhaust Temperature		Concentrations
	°K	°C	NH_3
$1NH_4Cl + 1LiAlH_4$	1069	796	4.7E-09
$1NH_4Cl + 2LiAlH_4$	828	555	2.1E-14
$1NH_4Cl + 3LiAlH_4$	645	372	9.9E-16
$1NH_4Cl + 4LiAlH_4$	537	264	1.2E-18

Recommended Formulation for Prototype Demonstration

$$NH_4Cl + 3LiAlH_4 \rightarrow LiCl + AlN + 2LiH + 2Al + 7H_2$$

Theoretical Yield 8.4%

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Hydrogen Gas-Generating Composition

$1NH_4Cl + 3Li\ AlH_4 + 1Mg(BH_4)_2 \cdot 2NH_3 + 4\%\ Fe_2O_3 + 3\%\ Kraton$

$\rightarrow LiCl + 2LiH + AlN + 2Al + 2BN + Mg + 14H_2$
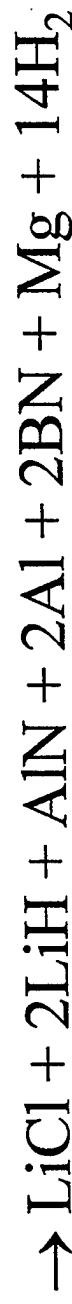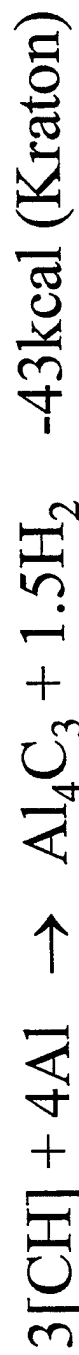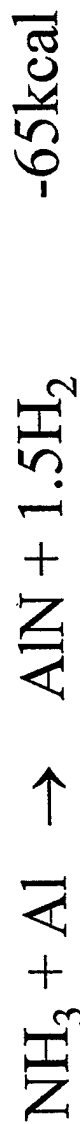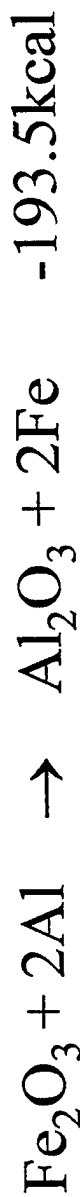
Theoretical Yield 10%

Requirements for a Hydrogen Gas Generator System

- Mechanical Properties/Porosity of Pressed Pellet

- Burning Rate

- Product of Reaction(Residue/Particulates)

- Temperature of Reaction

- Temperature of Reaction Chamber

Recommended Formulation for Prototype Demonstration

$$NH_4Cl + 3LiAlH_4 \rightarrow LiCl + AlN + 2LiH + 2Al + 7H_2$$

Side Reactions:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe \qquad -193.5kcal$$

$$NH_3 + Al \rightarrow AlN + 1.5H_2 \qquad -65kcal$$

$$3[CH] + 4Al \rightarrow Al_4C_3 + 1.5H_2 \qquad -43kcal \ (Kraton)$$

Hydrogen Gas-Generating Composition

$$1NH_{4Cl} + 3LiAlH_4 + 4\% \ Fe_2O_3 + 4\% \ C_3H_4$$
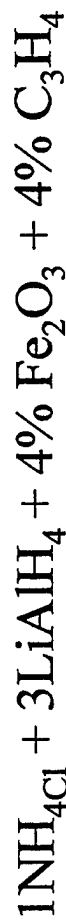
Reaction Chamber (number mols per 100g)

3.94546 H2	1.06299 LiH&	0.74429 Al&	0.54928 AlN&
0.54928 LiCl*	0.07967 Al4C3&	0.06049 CH4	0.05009 Fe&
0.03757 LiAlO2&	0.00000 Li2Cl2	0.00000 LiCl	0.00000 Li3Cl3
7.2E-08 LiH	3.47E-08 Li	4.79E-11 H	2.96E-11 C2H4
1.81E-11 AlH	1.42E-11 CH3	4.78E-12 AlCl	1.68E-12 Li2
1.37E-12 HCl	2.82E-14 Al	7.62E-15 NH3	

Exhaust Gas (number mols per 100g)

4.06313 H2	1.06299 LiH&	0.66584 Al&	0.54928 AlN&
0.54928 LiCl&	0.09929 Al4C3&	0.05009 Fe&	0.03757 LiAlO2&
1.65E-03 CH4	1.43E-13 Li2Cl2	8.03E-14 LiCl	1.55E-14 Li3Cl3

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Hydrogen Gas-Generating Composition

$1NH_4Cl + 3LiAlH_4 + 4\%$ Kraton

Pellets Pressed for:

- Burn Rate Measurements: $\sim$0.05 inch/sec (100psi)

- Gas Generation Demonstration (Parr Bomb)

  - Hydrogen
  - Ammonia
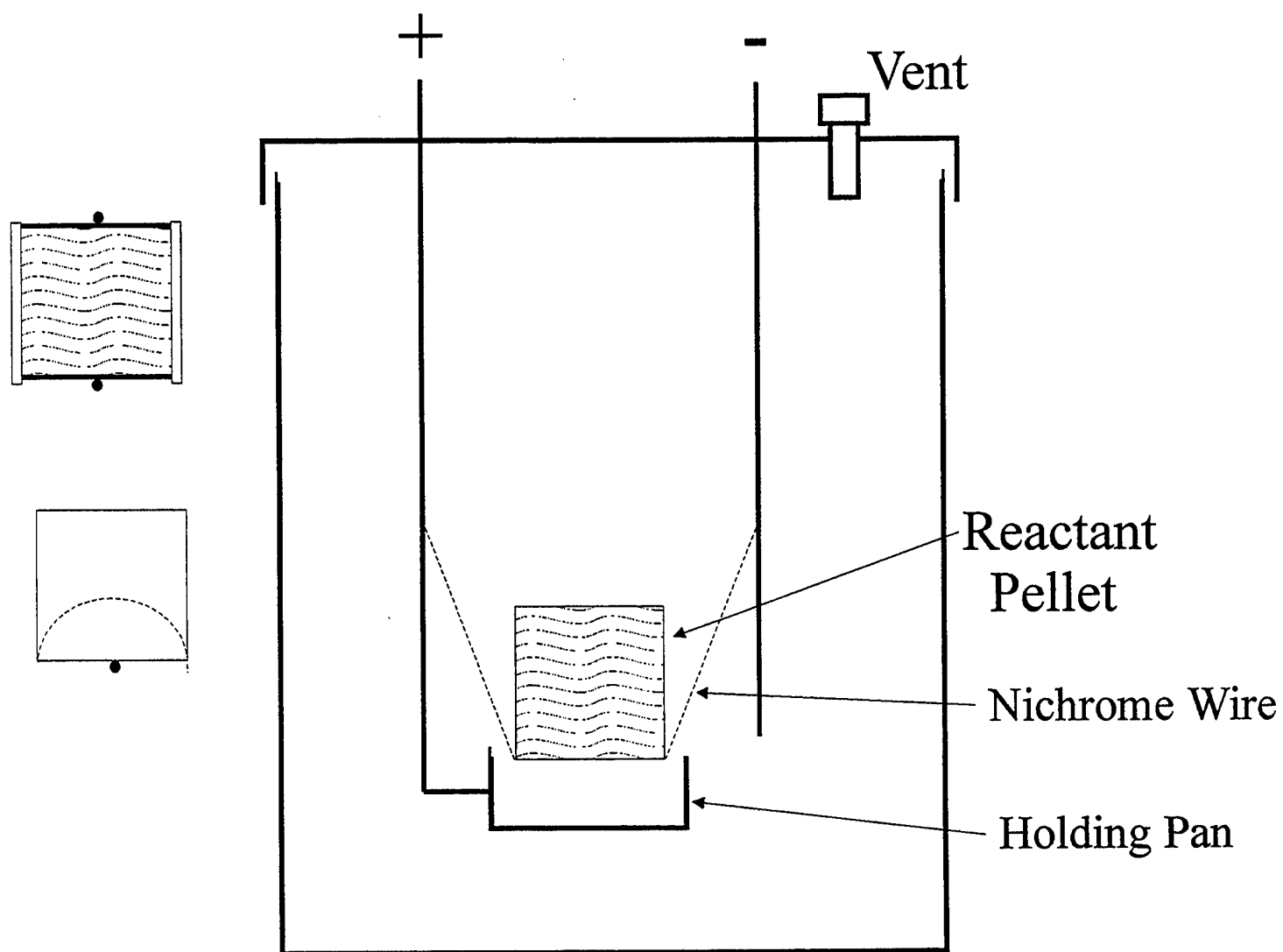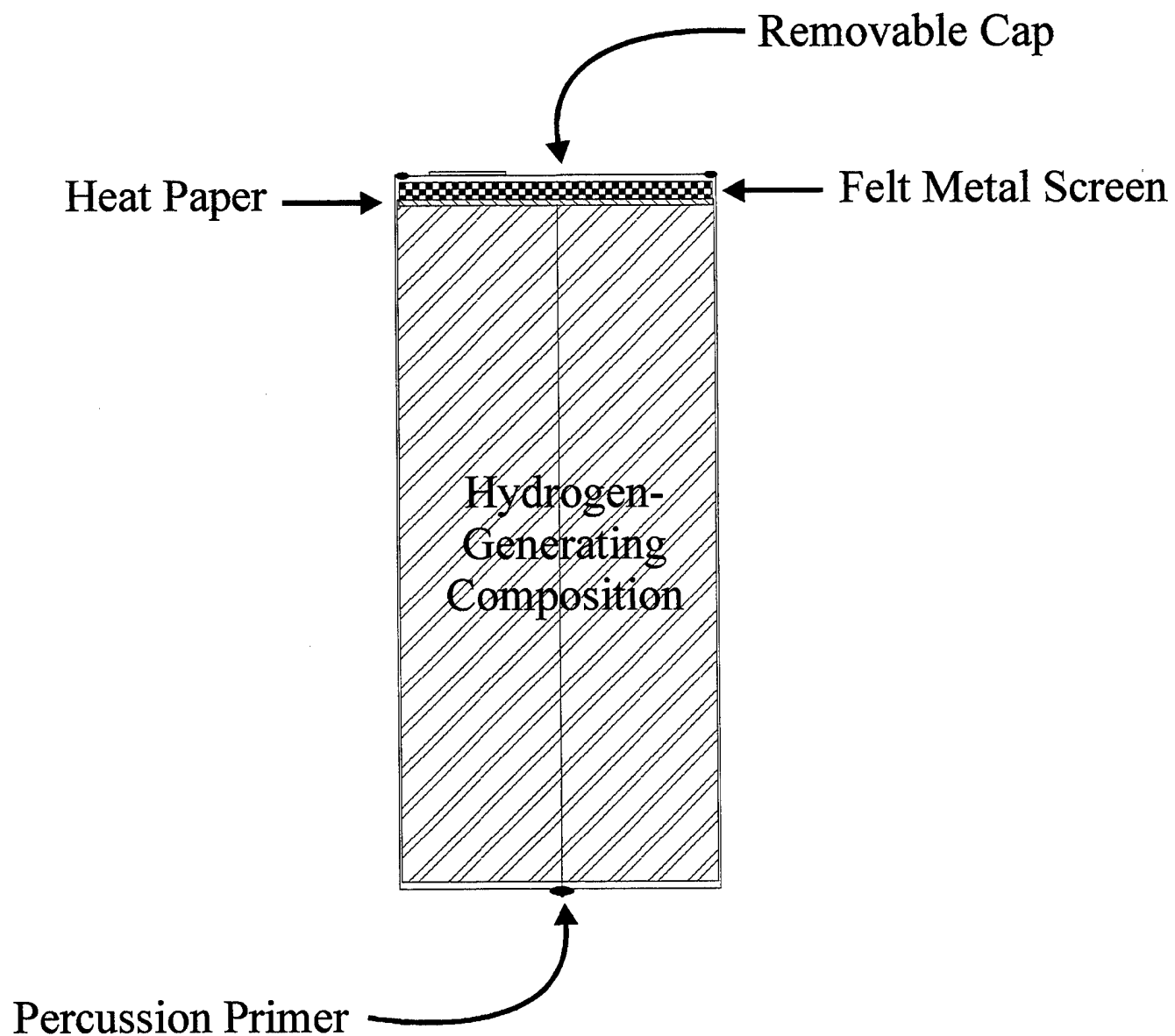
131

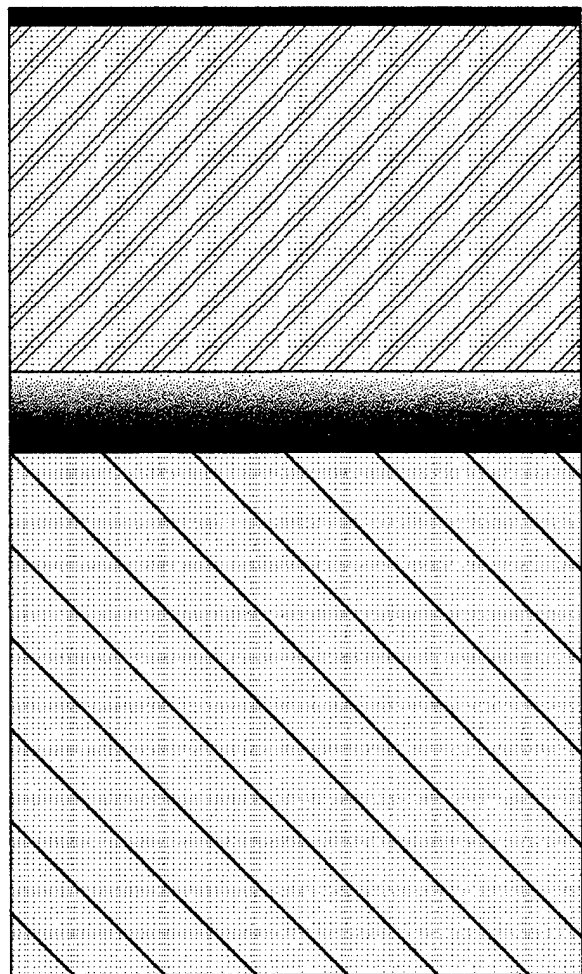# Hydrogen Generator Parr Bomb Test

Reactant Pellet

Nichrome Wire

Holding Pan

Vent

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Figure 3
Reactant Cartridge
(Royal Systems Design)

Removable Cap

Heat Paper →

← Felt Metal Screen

Hydrogen-Generating Composition

Percussion Primer —

Hydrogen Gas Generator Reaction Process

Heat Paper

Residue/Porous Clinker
$LiCl + AlN + 2LiH + 2Al$
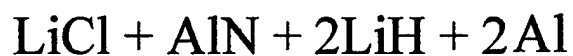
Reaction Zone: Hydrogen & Intermediate Products

Reactant Mixture
$NH_4Cl + 3LiAlH_4$
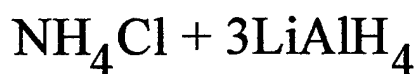
Ignition of Hydrogen Gas-Generating Composition

Ignition for End-Burning Configuration

Heat Paper (KDI - Score)

- Zirconium & Barium Chromate embedded in Glass Fiber processed into adhesive sheet approximately 1 mm thick

- Supplied Wet

- Specifications:

  Burning Rate: 17.78 cm/sec

  Heat Release: 37.12 cal/cm^2 (385 cal/g)

  Ignition Temperature: approximately 245 °C

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Figure 2
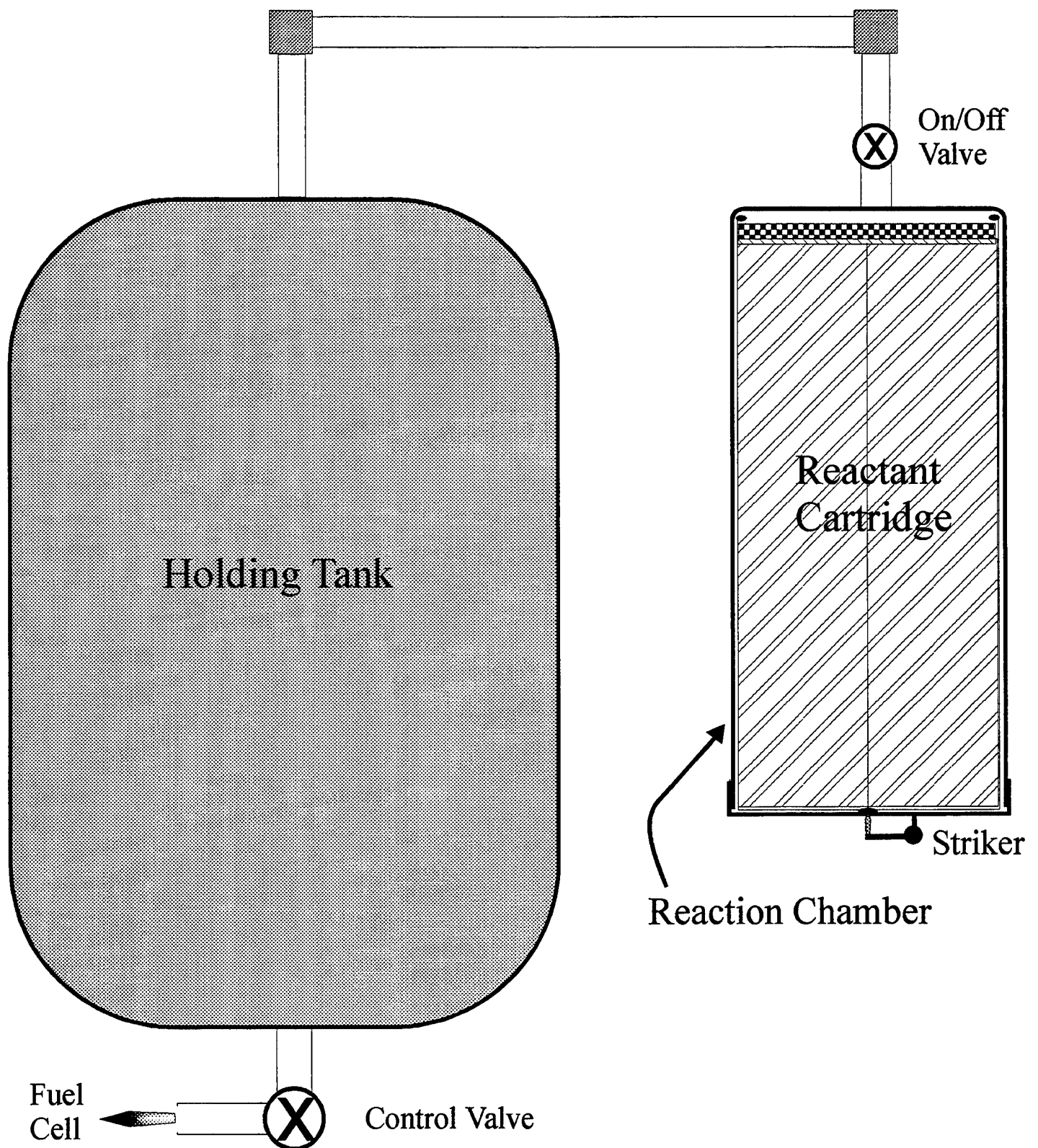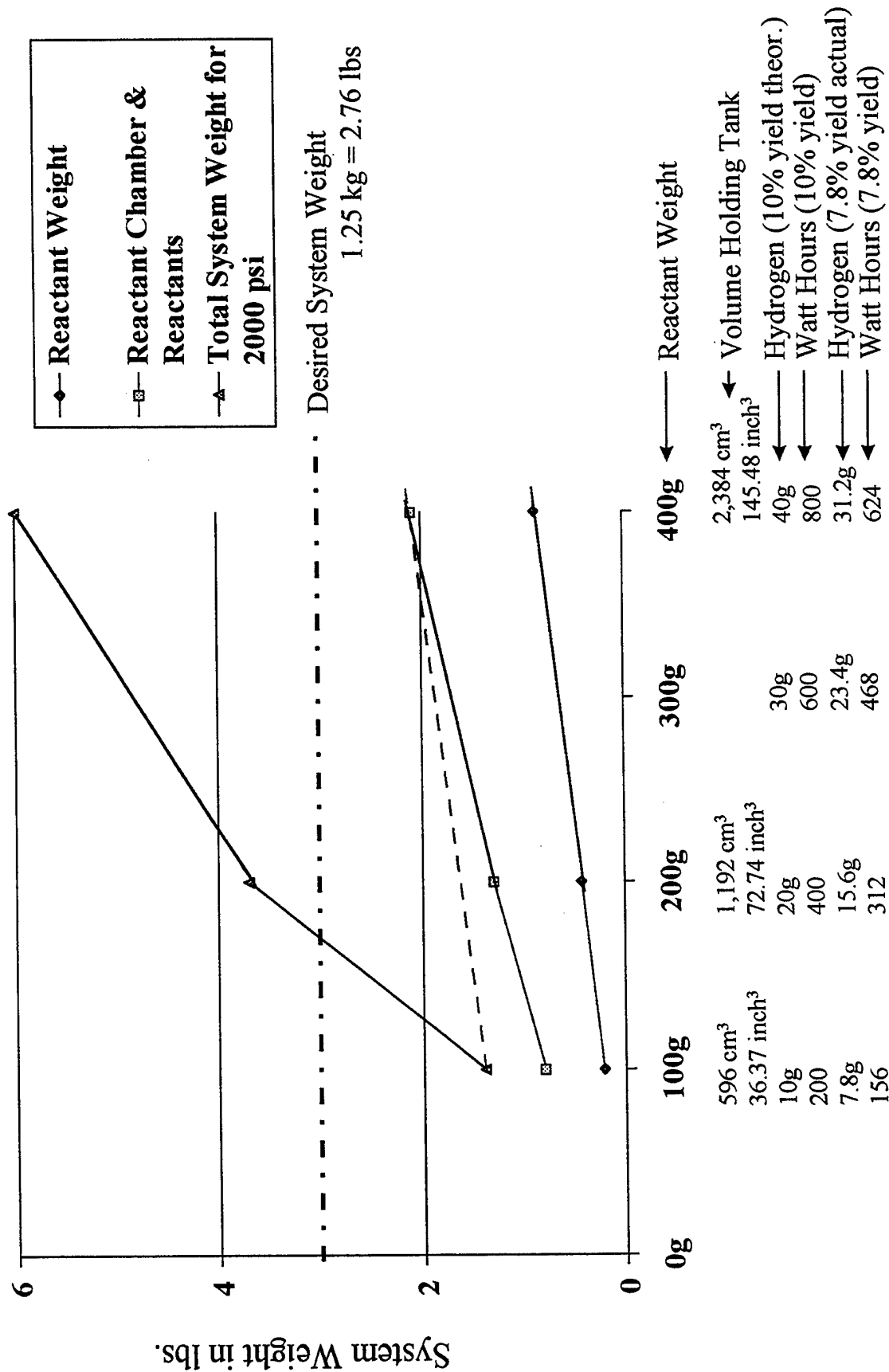## Hydrogen Gas-Generating System
(Royal Systems Design)

On/Off Valve

Reactant Cartridge

Holding Tank

Striker

Reaction Chamber

Fuel Cell

Control Valve

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Figure 5
System Weight vs. Reactant Weight
Hydrogen Gas Generator System
(Valves not included)

	0g	100g	200g	300g	400g	
Reactant Weight					400g	
Volume Holding Tank		596 cm³	1,192 cm³		2,384 cm³	
		36.37 inch³	72.74 inch³		145.48 inch³	
Hydrogen (10% yield theor.)		10g	20g	30g	40g	
Watt Hours (10% yield)		200	400	600	800	
Hydrogen (7.8% yield actual)		7.8g	15.6g	23.4g	31.2g	
Watt Hours (7.8% yield)		156	312	468	624	

Legend:
- Reactant Weight
- Reactant Chamber & Reactants
- Total System Weight for 2000 psi
- Desired System Weight 1.25 kg = 2.76 lbs

System Weight in lbs.

NOVEL ORGANOSILANES AS A UNIQUE HYDROGEN SOURCE FOR UNATTENDED FUEL CELLS WITH LOW THERMAL SIGNATURE

SRI International proposes to develop a novel hydrogen subsystem for a fuel cell power source capable of six months to five years of unattended life. Most current portable fuel cells are based on metal hydrides as the source of hydrogen. However, some of these hydrides are toxic, pose a severe explosion hazard, and must be stored in very heavy or very expensive storage devices. Also they are highly inefficient or require heating to higher temperatures to release hydrogen.

SRI's novel approach is to generate hydrogen from the catalytic reaction of high energy density organosilanes with water in a nonpassivating, homogeneous liquid phase. The organosilanes selected will not pose serious handling problems. Suitable organometallic catalysts will also be developed to moderate or promote the reactivity of organosilanes.

The proposed silanes will be incorporated into a lightweight subsystem for fuel cell power sources capable of six months to five years of unattended life. Because these silanes have theoretical energy densities higher than any other metal hydride or hydride alloy used so far, they represent a superior source of hydrogen. In addition, they are liquid and therefore are not expected to suffer any passivation during hydrogen production. We will select silanes and catalysts to develop a system with a low thermal signature of hydrogen production, and any produced water will be recycled for hydrolysis so that water disposal will not be necessary. In our opinion, these features make the proposed silanes largely superior to any metal hydride or hydride alloy.

Silanes are an excellent source of hydrogen and have a higher energy density than either the metal hydrides or the hydride alloys. Although silane (SiH_4) is a pyrophoric gas, silane derivatives obtained by introducing aromatic or ethynyl groups into silanes have drastically reduced reactivity and can be handled conveniently. The reactivity of an organosilane depends on the nature of other functionalities present in the molecule and can thus be tailored to specifications to a certain extent.

We propose to synthesize organosilanes that will be stable, efficient sources of hydrogen for unattended fuel cells. These organosilanes must (1) either be a liquid or form a low melting eutectic with another silane, (2) not be pyrophoric, (3) have a moderate

reaction with water (in the presence of a catalyst) to liberate hydrogen, and (4) not suffer from passivation during hydrogen production.

A few silanes that meet the criteria given above have been selected for the production of hydrogen for the fuel cells. Most of these silanes have been synthesized and spectrally characterized and show a high efficiency of hydrogen production. For example, ethenyl silane, ethynyl silane, and phenyl silanes are excellent sources of hydrogen. Because these silanes are liquids, they react in a homogenous fashion with water in the presence of a catalyst to provide a clean, efficient source of hydrogen for remote fuel cells.

Our approach will be to synthesize silanes by conventional synthesis methods, taking into consideration the cost and efficiency of the synthesis procedures. All the proposed syntheses are either well documented in the literature or will be conducted according established synthesis procedures.

Several catalysts will be evaluated for promoting hydrogen generation for the highest possible power rate required for the desired application. Metallorganic catalysts, strong acids (e.g., triflic acid), or bases will be tested as catalysts and evaluated for their efficiency.

Kinetics studies will be performed to determine the rate of hydrogen production as a function of silane structure, catalyst, and rate of mixing. We will examine the efficiency of hydrogen production and perform a thorough study of any passivation issues. The system will be optimized so that all the water produced in the fuel cell for power production is completely used for hydrogen generation.

A complete subsystem for hydrogen production to be incorporated into a lightweight fuel cell stack will be eventually developed. This subsystem will also be used for our kinetics studies.

The tabulation below compares some of the selected silanes with metal hydrides for their efficiency of hydrogen production.

Silanes	Efficiency Hydrogen Production
$(H_3Si)_2C=(SiH_3)_2$	9.4
$C(SiH_3)_4$	9.8
$H-C\equiv C-SiH_3$	7.2
$H_3Si-C\equiv C-SiH_3$	8.6
$C_6H_5SiH_3$	4.4
$C_6H_4(SiH_3)_2$	6.2

$C_6H_3(SiH_3)_3$	7.2
$C_6(SiH_3)_6$	8.6
Metal hydrides	
$NaBH_4$	7.3
$NaAlH_4$	6.4

NOVEL ORGANOSILANES AS A UNIQUE HYDROGEN SOURCE FOR UNATTENDED FUEL CELLS WITH LOW THERMAL SIGNATURE

by

SUBHASH NARANG
SUSANNA VENTURA
MARY REPPY
DURGA ANNAVAJULA
KK BHASIN
SUNITI SHARMA

SRI INTERNATIONAL

SILANES FOR HYDROGEN PRODUCTION

- SRI'S APPROACH IS TO GENERATE HYDROGEN FROM THE CATALYTIC REACTON OF HIGH ENERGY DENSITY ORGANO SILANES WITH WATER IN A NON PASSIVATNG HOMOGENEOUS LIQUID PHASE

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PROGRAM OUTLINE

Task 1. Synthesis of Silanes.

High-energy density silanes for hydrogen production will be synthesized. Selection criteria for the proposed silanes include (1) high efficiency of hydrogen production (2) safe handling (3) moderate controlled reaction with water and (4) no passivation during hydrogen production.

Task 2. Selection of Catalysts.

Several catalysts will be evaluated for promoting hydrogen generation for the highest possible power rate required for the desired application. Organometallics, strong acids and bases will be evaluated.

Task 3. Kinetic Studies for Hydrogen Generation.

We will study the rate of hydrogen production as a function of the silane structure, catalyst and rate of mixing. Efficiency of hydrogen production and any passivation issues will be evaluated.

Task 4. Microcalorimetry.

We will use microcalorimetry to measure the heat of hydrolysis reaction of the selected silanes. This study will help us to select silanes with low thermal signature.

Task 5. Subsystem Development.

We will develop and test a subsystem for hydrogen productionb to be incorporated into unattended fuel cells
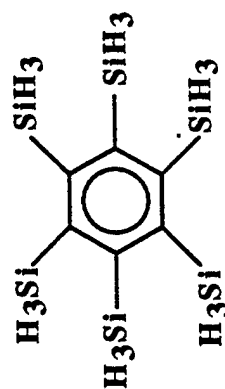
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ORGANO SILANES

- AIR STABLE
- STABLE IN WATER ?
- LIQUID
- STOICHIOMETRIC REACTION WITH WATER
- EFFICIENT HYDROGEN PRODUCTION AT ROOM TEMPERATURE
- REACTION APPEARS TO BE THERMONEUTRAL ?
- NON PASSIVATING SYSTEM
- CAN BE INCORPORATED IN A COMPACT SUBSYSTEM
- THROTTLING OF HYDROGEN PRODUCTION POSSIBLE ?
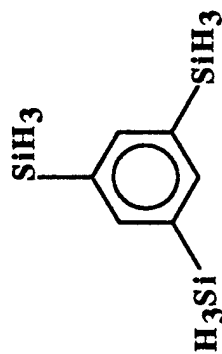
144

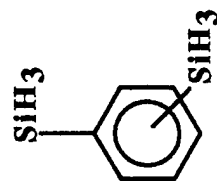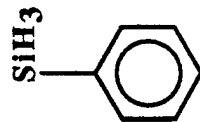# PROPOSED SILANES

(EFFICIENCY OF HYDROGEN PRODUCTION)
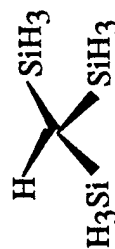
$H_3SiC \equiv CSiH_3$

(8.6)

$HC \equiv C(SiH_3)$

(7.2)

$(H_3Si)_2C = C(SiH_3)_2$

(9.4)

(9.8)

(9.6)

(4.4)

(6.2)

(7.2)

(8.6)

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EFFICIENCY OF HYDROGEN PRODUCTION

$$C(SiH_3)_4 \ + \ 6H_2O \ \longrightarrow \ C(SiOO_{1/2})_4 \ + \ 12H_2$$

STOICHIOMETRIC WEIGHTS OF REACTANTS AND PRODUCTS :

$$(136) \qquad (108) \qquad\qquad (220) \qquad (24)$$
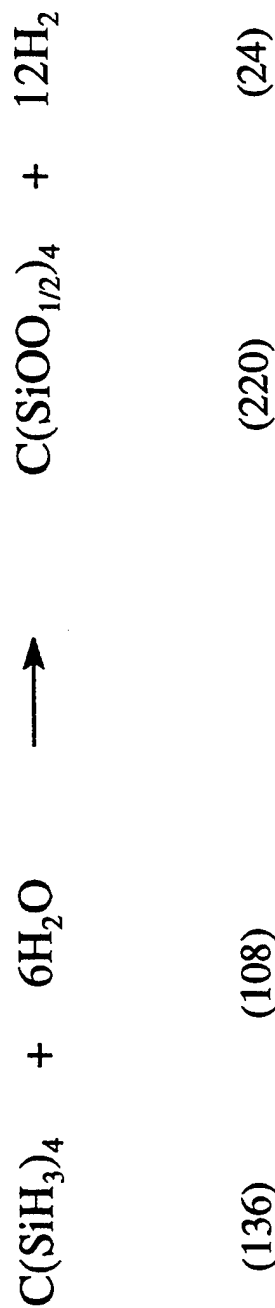
EFFICIENCY OF
HYDROGEN PRODUCTION = 100X (WEIGHT OF H_2)/ (WEIGHT OF REACTANTS)

$$= \ 100X(24)/(136 + 108) \ = \ 9.8\%$$

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EFFICIENCY OF HYDROGEN PRODUCTION

$$NaBH_4 \;+\; 4H_2O \longrightarrow NaOH \;+\; B(OH)_3 \;+\; 4H_2 \qquad (8)$$
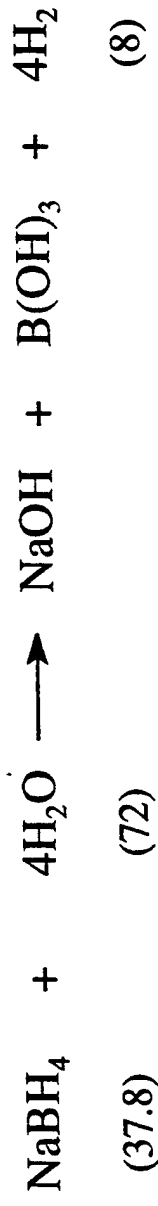
$(37.8) \qquad (72)$

EFFICIENCY OF
HYDROGEN PRODUCTION = $100X(8)/(37.8+72)$ = 7.3%

$$LiBH_4 \;+\; 4H_2O \longrightarrow LiOH \;+\; B(OH)_3 \;+\; 4H_2 \qquad (8)$$

$(21.7) \qquad (72)$

EFFICIENCY OF
HYDROGEN PRODUCTION = $100X(8)/(21.7+72)$ = 8.5%

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EFFICIENCY OF HYDROGEN PRODUCTION

Silanes

$C(SiH_3)_4$	9.8
$(H_3Si)2C = C(SiH_3)_2$	9.4
$H_3Si-C \equiv C-SiH_3$	8.6
$C_6(SiH_3)_6$	8.6
$HC \equiv CSiH_3$	7.2
$C_6H_3(SiH_3)_3$	7.2
$C_6H_4(SiH_3)_2$	6.2
$C_6H_5SiH_3$	4.4

Metal hydrides

$LiBH_4$	8.6
$NaBH_4$	7.3
$NaAlH_4$	6.4

SPECIFIC CAPACITY OF ORGANOSILANES AND METAL HYDRIDES (Ah/gm of reactants)

$C(SiH_3)_4$	2.63	$LiBH_4$	2.29
$HC(SiH_3)_3$	2.57	LiH	2.06
$(H_3Si)_2CC(SiH_3)_2$	2.51	$LiAlH_4$	1.95
$H_3SiCCSiH_3$ & $C_6(SiH_3)_6$	2.29	$NaBH_4$	1.95
$C_6H_3(SiH_3)_3$	1.94	KBH_4	1.70
$HCCSiH_3$	1.93	CaH_2	1.37
$C_6H_4(SiH_3)_2$	1.67		
$C_6H_5SiH_3$	1.48		

SPECIFIC CAPACITY

BASIS OF CALCULATION: AMOUNT OF MATERIAL REQUIRED TO PRODUCE
ONE EQUIVALENT OF HYDROGEN

$$LiBH_4 + 4H_2O \longrightarrow 4H_2 + LiOH + B(OH)_3$$

**STOICHIOMETRIC
WEIGHTS OF
REACTANTS AND
PRODUCTS :**   (21.7)   (72)   (8)   (23.9)   (61.8)

AMOUNT OF MATERIAL REQUIRED
TO PRODUCE ONE EQUIVALENT
OF HYDROGEN:

$$(21.7) + 72)/(8) = 11.7gm = 26.8Ah$$

SPECIFIC CAPACITY (Ah/gm)   = 2.29

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SPECIFIC CAPACITY OF ORGANOSILANES

$$C(SiH_3)_4 \quad + \quad 6H_2O \quad \longrightarrow \quad C(SiOO_{1/2})_4 \quad + \quad 12H_2 \qquad (24)$$

$$(136) \qquad\qquad (108) \qquad\qquad\qquad (220)$$

STOICHIOMETRIC WEIGHTS OF REACTANTS AND PRODUCTS :

SPECIFIC CAPACITY (Ah/gm) = (26.8)/ [(136 + 108)/24] = 2.63

|5|

DISILYL ACETYLENE

$$LiC \equiv CLi \quad + \quad SiCl_4 \quad \xrightarrow[\text{RT}]{\text{THF/MONOGLYME}} \quad Cl_3SiC \equiv CSiCl_3$$

$$Cl_3SiC \equiv CSiCl_3 \quad + \quad LiAlH_4 \quad \xrightarrow[]{\text{Ether, RT}} \quad H_3SiC \equiv CSiH_3$$

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TETRA SILYLMETHANE

$C(SiH_3)_4$

$SiH_3-C_6H_5 + SnCl_4 \longrightarrow SiH_2Cl-C_6H_5 + SnCl_2 + HCl$

$CBr_4 + PhSiH_2Cl + 4Mg \longrightarrow C(SiH_2Ph)_4 + 4MgCl$

$C(SiH_3)_4 \xleftarrow{LiAlH_4} C(SiH_2Br)_4 \xleftarrow[HBr]{-78C}$

$HC(SiH_3)_3 \xleftarrow[LiAlH_4]{-SiH_4}$
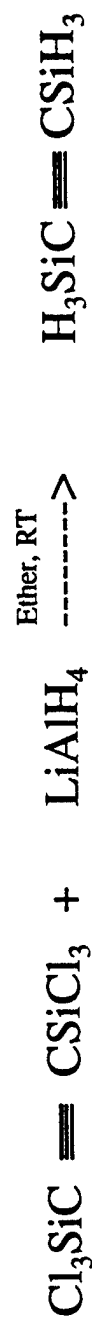
ALTERNATIVE SYNTHESIS OF
TETRA SILYLMETHANE
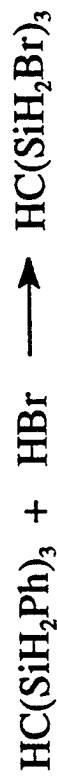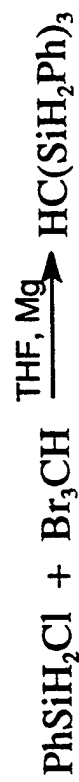
$$CL_4 \xrightarrow{\text{BrSiH}_3} C(SiH_3)_4$$

SIMILAR PROCEDURE FOR

DISILYLACETYLENE
TETRA SILYLETHYLENE

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ALTERNATE SYNTHESIS OF
TETRA SILYL METHANE

$$SiCl_4 \ + \ 3Si(OCH_3)_4 \ \xrightarrow{AlCl_3} \ 4ClSi(OCH_3)_3$$

$$C(Si(OCH_3)_3)_4 \ + \ LiAlH_4 \ \xrightarrow{\text{TETRA HYDRONAPHTHALENE}} \ C(SiH_3)_4$$

TRISILYL METHANE

$PhSiH_3 + SnCl_4 \longrightarrow PhSiH_2Cl + SnCl_2 + HCl$

$PhSiH_2Cl + Br_3CH \xrightarrow{THF,\ Mg} HC(SiH_2Ph)_3$

$HC(SiH_2Ph)_3 + HBr \longrightarrow HC(SiH_2Br)_3$

$HC(SiH_2Br)_3 + LiAlH_4 \longrightarrow HC(SiH_3)_3$
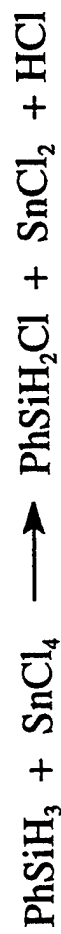
1,4-DISILYLBENZENE

1,3,5-TRIS(SILYL BENZENE)

Mg, THF
CISi(OMe)3

LiAlH4
Et2O, 0C

HEXASILYLBENZENE

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X: CF₃SO₃

161
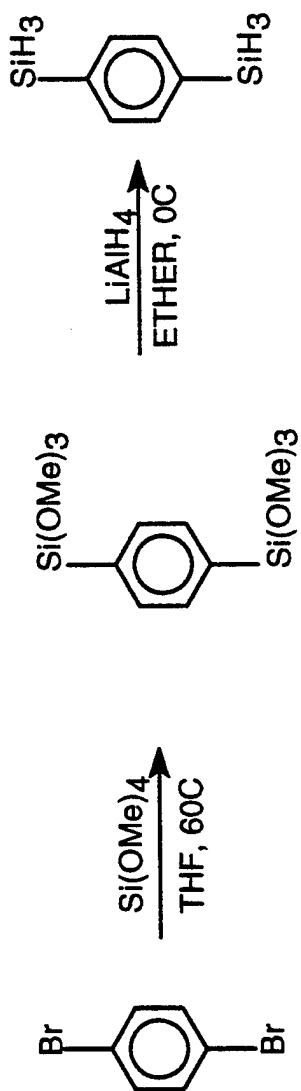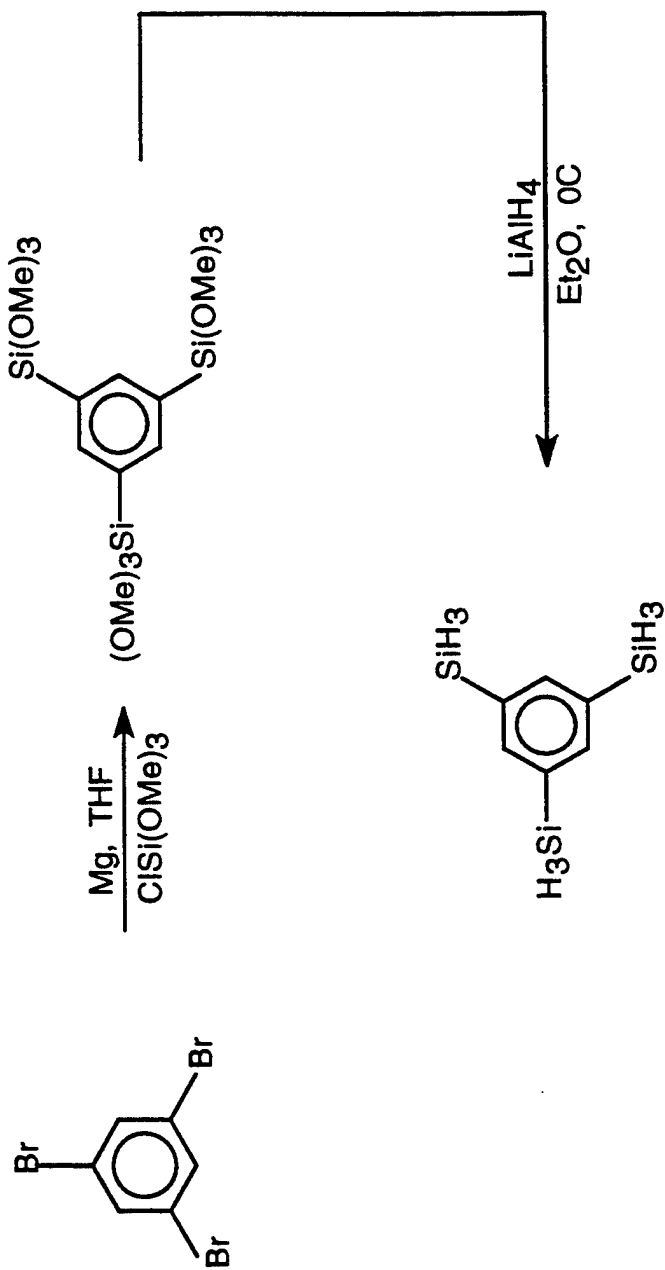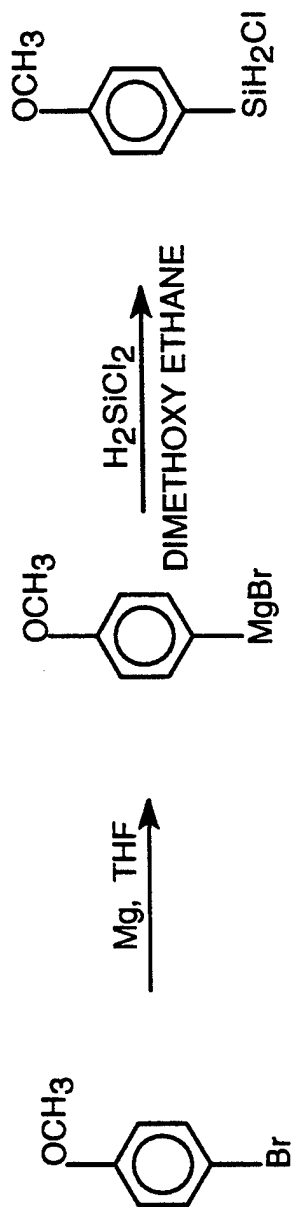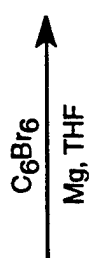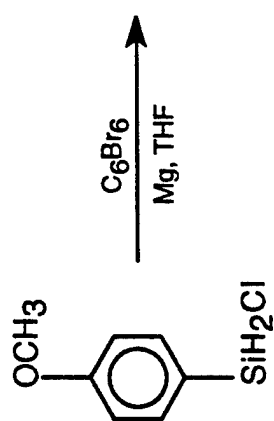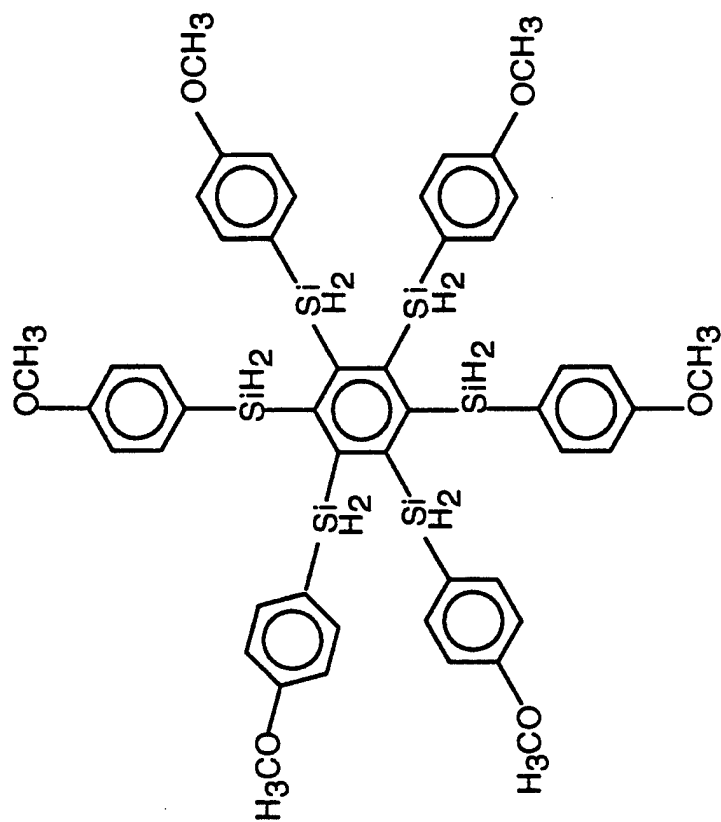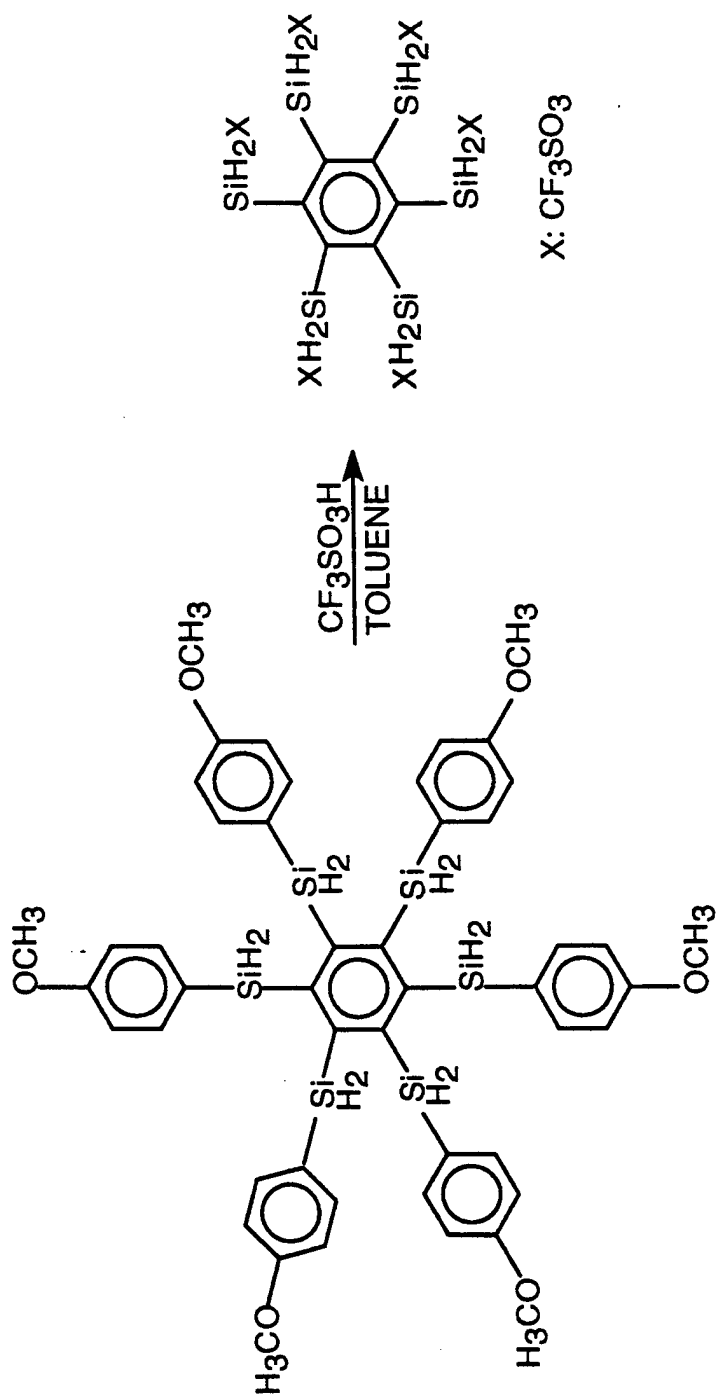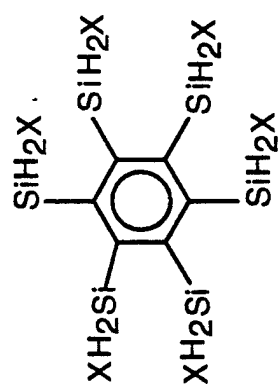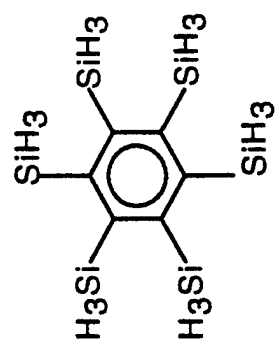
X: CF₃SO₃

ALTERNATIVE SYNTHESIS OF HEXASILYLBENZENE

163
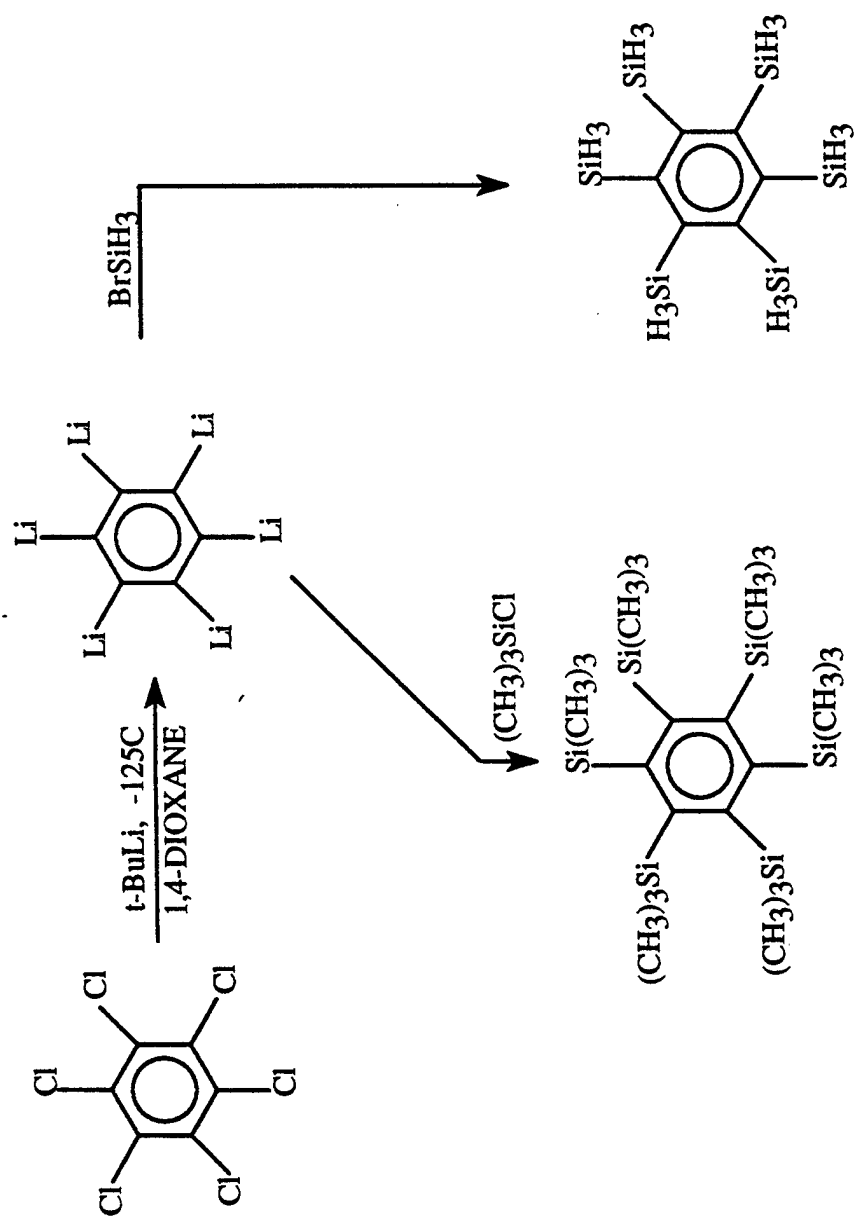
HYDROLYSIS EXPERIMENTS

PHENYL SILANE

SiH$_3$—C$_6$H$_5$ + H$_2$O $\xrightarrow[\text{TEMPERATURE}]{\text{ROOM}}$ HYDROGEN GENERATION < 5%

SiH$_3$—C$_6$H$_5$ + 10% NaOH/WATER $\xrightarrow[\text{TEMPERATURE}]{\text{ROOM}}$ HYDROGEN GENERATION > 98%

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HYDROLYSIS EXPERIMENTS
TRISILYL METHANE

HC(SiH₃)₃ + H₂O $\longrightarrow$ <5% REACTION

HC(SiH₃)₃ + NaOH $\longrightarrow$ <5% REACTION
(20% IN WATER)

HC(SiH₃)₃ + NaOH $\xrightarrow{\text{ROOM TEMPERATURE}}$ > 75 % HYDROGEN GENERATION
20 % IN **(VERY FAST REACTION)**
A 1:1 MIXTURE
OF WATER AND METHANOL

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HYDROLYSIS EXPERIMENTS
TRISILYL METHANE

$HC(SiH_3)_3$ + H_2O $\longrightarrow$ <5% REACTION

$HC(SiH_3)_3$ + NaOH $\longrightarrow$ <5% REACTION
(20% IN WATER)

$HC(SiH_3)_3$ + NaOH $\xrightarrow{\text{ROOM TEMPERATURE}}$ > 75 % HYDROGEN GENERATION **(VERY FAST REACTION)**
20 % IN
A 1:1 MIXTURE
OF WATER AND METHANOL

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HYDROLYSIS EXPERIMENTS
TRISILYL METHANE

HC(SiH₃)₃   + NaOH
20% IN WATER
0.1% LAS
⟶ 20% REACTION

HC(SiH₃)₃   + NaOH
20% IN WATER, THF
⟶ >75% REACTION

HC(SiH₃)₃   + NaOH
20% IN WATER,
THF, 0.1%LAS
⟶ >75% REACTION

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MODEL REACTIONS

HYDROLYSIS OF HEXYLSILANE, $C_6H_{13}SiH_3$

$H_2O + C_6H_{13}SiH_3 \longrightarrow$ NO REACTION

$20\% \ NaOH + C_6H_{13}SiH_3 \longrightarrow$ NO REACTION

$CH_3OH + C_6H_{13}SiH_3 \longrightarrow$ NO REACTION

$isoC_3H_7OH + C_6H_{13}SiH_3 \longrightarrow$ NO REACTION

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HYDROLYSIS OF HEXYLSILANE, $C_6H_{13}SiH_3$

20% NaOH + CH_3OH $\longrightarrow$ >98% HYDRGEN GENERATION, Very Fast

20% NaOH + isoC_3H_7OH $\longrightarrow$ >98% HYDROGEN GENERATION, Moderate

20% NaOH + 0.2% Surfactant $\longrightarrow$ 60% HYDROGEN GENERATION, Slow

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FUTURE WORK

- SYNTHESIZING BIGGER AMOUNTS OF TETRA SILYL METHANE
- KINETICS OF CONTROLED HYDROLYSIS OF ALKYL AND PHENYL SILANES
- USE OF CATALYST TO TAILOR THE KINETICS OF HYDROLYSIS
- INCORPORATING THE SILANES IN TO THE SUBSYSTEM
- INVESTIGATION OF HIGHER ENERGY DENSITY BORANES

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BORANES

HYDROGEN EFFICIENCY BY % WEIGHT OF REACTANTS
(STOICHIOMETRIC WATER)

$C(BH_2)_4 + 4H_2O \longrightarrow C(BO)_4 + 8H_2$ $(100X16)/(63.2 + 72) = 11.83$

$C_6(BH_2)_6 + 6H_2O \longrightarrow C_6(BO)_6 + 12H_2$ $(100X24)/(148.8 + 108) = 9.34$

$2BH_3.N(SiH_3)_3 + 7H_2O \longrightarrow B_2O_3 + 2NH_3 + 2SiO_2 + 16H_2$

$(100X32)/(241.6 + 126) = 8.70$

$C(SiH_3)_4 + 6H_2O \longrightarrow C(Si(OO_{1/2}))_4 + 12H_2$
$(100X24)/(136 + 108) = 9.8$

$2BH_3.O(SiH_3)_2 + 9 H_2O \longrightarrow B_2O_3 + 4SiO_2 + 18H_2$ $(36X100)/(92X2 + 9X18) = 10.4$

$2BH_3.O(BH_2)_2 + 7H_2O \longrightarrow 3B_2O_3 + 14H_2$ $(28X100)/(56X2 + 7X18) = 11.7$

170
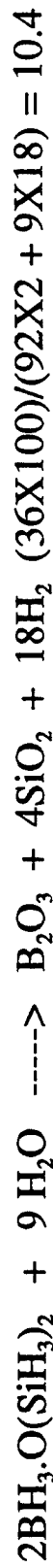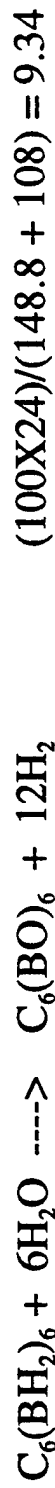
Hydrogen Storage Using Decalin

X. Lu, W. Li, A. Franco, and R.O. Loutfy

Materials and Electrochemical Research Corporation, Tucson, AZ 85706

Abstract

In this study, the feasibility of high-density hydrogen storage system using decalin has been investigated. Decalin-naphthalene system has 7.25% by weight theoretical hydrogen capacity, and hydrogen charge-discharge on the system is based on the catalytic hydrogenation and dehydrogenation processes. Experimental results showed that hydrogen can be reversibly charged and discharged to/from decalin system at moderate temperatures, over 77% decalin-naphthalene conversion can be achieved at 260°C.

Background

Research work indicated that for a small to medium fuel cell power generation system (up to few thousand watt), the ideal hydrogen storage methods are the ones based on the chemical hydrides [1-3]. Chemical hydrides can be divided into solid chemical hydrides and liquid hydrides. Typical solid hydrides are lithium borohydride ($LiBH_4$), lithium aluminum hydride ($LiAlH_4$), and organo-silane ($C_6H_5SiH_3$); while typical liquid hydrides are methylcyclohexane ($C_6H_{11}CH_3$) and decahydronaphthalene ($C_{10}H_{18}$, usually called decalin).

The advantage to use chemical hydride for hydrogen storage is the high densities. All the chemical hydrides mentioned above can release about 6 to 8.5% by weight hydrogen gas, and the volumetric densities range from 47 to 65 kg H_2/m^3, which are higher than liquefied hydrogen system (~45 kg H_2/m^3) as shown in **Table I**. These storage capacities are far better than those of metal hydrides which only have less than 1.5% by weight of hydrogen capacities [4].

Table I. Hydrogen storage based on chemical hydrides and on liquefied H_2

Storage Mode	Gravimetric Density (wt%)	Volumetric Density (kg/m^3)	Temperature (°C)	Reversi-bility	Cost of Hydride* ($/kg)
Solid Hydride $LiBH_4 + 4H_2O$	8.54	56.9	un-control-able	No	4,336.
Liquid Hydride $C_{10}H_{18}$ (Decalin)	7.25	64.96	~250	Yes	34.38
Liquid Hydride $C_6H_{11}CH_3$ (Methylcyclohexane	6.12	47.12	~250	Yes	42.01
Liquefied Hydrogen	~20	40~50	-253	Yes	--

* Aldrich Catalog, 1995-1996

The hydrogen storage using decalin is based on the catalytic hydrogenation and dehydrogenation process. Therefore, the hydrogen storage system is a reversible one, being able to be recharged by catalytic hydrogenation. The reversible chemical reaction of decalin dehydrogenation-hydrogenation is illustrated as follows:

C10H18(Decalin)   C10H8(Naphthalene)
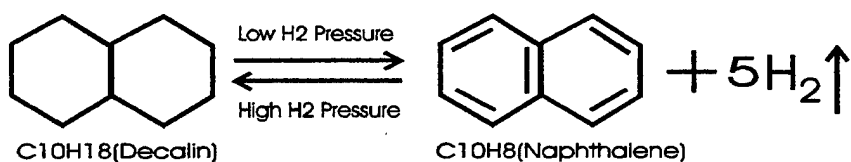
Compared with systems based on solid chemical hydrides, other liquid organic hydrides, and metal hydrides, the hydrogen storage system based on decalin has the following advantages (see **Table I** for the comparison):

1. Higher storage capacities, especially the volumetric density.
2. Much easier to control hydrogen release rate, release pressure, and to turn on and off the hydrogen supply when required.
3. No complicated auxiliary systems are required.
4. Reversible of hydrogen charge and discharge processes, no chemical wastes are generated.
5. Less expensive, the cost of liquid hydrides is more than 100 times less than that of solid chemical hydrides.

Results and Discussion

To study hydrogen charge-discharge properties, a mini-batch catalytic reactor was designed and constructed to study decalin hydrogenation and dehydrogenation processes. A Johnson-Mattey thin membrane hydrogen filter was purchased for hydrogen/liquid hydride vapor separation. However, due to delay of filter shipment, a water cooling condenser was used for most of the experimental runs. It was found that with the membrane for hydrogen separation, the conversion of decalin to naphthalene is higher when other experimental conditions are the same.

In a typical decalin dehydrogenation run, 40 ml decalin and 0.5 - 1.0 g catalyst were used, the reaction temperature ranged from 240 to 260 °C, and the reaction was run for 3 to 5 hours. The hydrogenation of naphthalene was done in the same mini-reactor right after the dehydrogenation of decalin with reaction temperature of 180°C and hydrogen pressure of 10 atm. Various catalysts such as Pt, Ni, Pd and Rh supported on carbon or alumina have been used. It was found that although the Ni and Pd based catalysts are effective, the Pt on carbon catalyst is the best. The following results are all based on the reaction runs using 5% Pt on carbon catalyst.

For the dehydrogenation of decalin, at 260°C, about 18.5 liter hydrogen can be released from 40 ml decalin within 3 hours, which corresponds to a 64% conversion. Over 77% conversion can be achieved within 5 hours. The dehydrogenation reaction was

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found to be strongly temperature dependent. From the reaction runs at different temperature, the activation energy for decalin dehydrogenation was estimated to be 28.3 kJ/mole H_2, which means to release one mole of hydrogen gas from decalin, less than 28.3 kJ energy is required. This energy is equivalent to 9.96% of the higher heating value (HHV) of hydrogen gas. The flow rate during hydrogen release has also been regulated and no significant effect on the dehydrogenation process was observed.

To test the recyclability of the hydrogen charge-discharge of the decalin-naphthalene system, dehydrogenation and hydrogenation reaction cycles were conducted. A total of eleven cycles have been completed so far. The results showed that hydrogen can be reversibly released from and charged to the decalin hydrogen storage system. No significant performance deterioration was observed after 11 recycle runs.

Conclusions

It has been demonstrated that liquid-hydride decalin is feasible for high density hydrogen storage applications. The gravimetric and the volumetric densities of hydrogen on decalin are 7.25% and 65 kg/m^3, respectively. Effective hydrogen discharge can be achieved by using Pt based catalyst at 260°C, while hydrogen charge can be done at 180°C under 10 atm hydrogen pressure. The system has been shown to be simple, recyclable and inexpensive. While the results are encouraging and promising, more research work is needed before a practical hydrogen storage system can be developed.

Acknowledgment

References

1.   O.A. Velev, et al., "High density hydrogen storage and generation for proton exchange membrane fuel cells", paper preseneted at 189th ECS Meeting, Los Angeles, CA (1996).

2.   R.H. Manser Souderer, "Methylcyclohexane dehydrogenation kinetics, reactor design and simulation for a hydrogen powered vehicle", Ph.D. Dissertation, Eidgenoessisch Technische Hochschule, Zurich, Switzerland (1993).

3.   S. Srinivansan, et al., "Hydrogen generation from light weight hydrides", Presentation at the Hydrogen Generation Review Meeting for ORD, Arlington, Virginia, June 11 (1996).

4.   L. Schlapbach (editor), "Hydrogen in Intermetallic Compounds I", Spronger-Verlag, New York, NY (1988).

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MER Corporation, Tucson, Arizona

Hydrogen Storage Using Decalin

Workshop on Hydrogen Storage and Generation

Orlando, Florida   April 8-10, 1997

MER Corporation, Tucson, Arizona

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Outline

- Background

- Experiment

- Hydrogen Release

- Hydrogen Charge-Release Cycles

- Energy Balance and System Specifications

- Conclusions

Background

- Hydrogen storage using chemical hydrides has advantages of high capacity and low cost compared with metal hydrides

- The hydrogen storage capacities on chemical hydrides are comparable to those of liquefied hydrogen option

- Liquid organic hydrides are more economical and practical than solid chemical hydrides

-------Orlando Meeting, MER Corporation-------

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Comparison of hydrogen storage based on chemical hydrides and on liquefied H_2

Storage Mode	Gravimetric Density (wt%)	Volumetric Density (kg/m^3)	Temperature (°C)	Reversibility	Cost of Hydride* ($/kg)
Solid Hydride $LiBH_4 + 4H_2O$	8.54	56.9	uncontrollable	No	4,336.00
Liquid Hydride $C_{10}H_{18}$ (Decalin)	7.25	64.96	~250	Yes	34.38
Liquid Hydride $C_6H_{11}CH_3$ (Methycyclohexane)	6.12	47.12	~250	Yes	42.01
Liquefied Hydrogen	~20	40~50	-253	Yes	–

* Aldrich Catalog, 1995-1996

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Liquid Organic Hydrides

- Among liquid organic hydrides, two-benzene-ring-structured decalin (decahydronaphthalene $C_{10}H_{18}$) is superior to one-benzene-ring-structured or three-benzene-ring-structured organic hydrides

- Why? 1) Lower vapor pressure (<4 atm at 260C, over 20 atm for $C_6H_{11}CH_3$); 2) Higher hydrogen storage capacity; 3) Liquid phase at hydrogenation and dehydrogenation temperature (Anthracene is in solid phase at hydrogenation temperature)

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Principle

- The principle of hydrogen storage using decalin is based on catalytic dehydrogenation and hydrogenation:

C10H18(Decalin) → C10H8(Naphthalene) + 5H$_2$

Low H2 Pressure

High H2 Pressure

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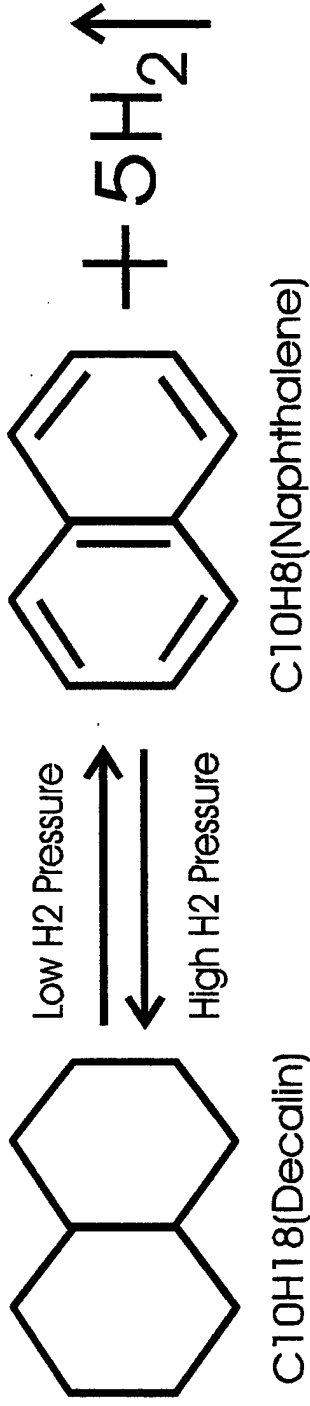
Experiment

- A mini-batch catalytic reactor was designed and constructed to study decalin hydrogenation and dehydrogenation processes

- A Johnson-Mattey thin membrane hydrogen filter was purchased for hydrogen/liquid hydride vapor separation. However, due to delay of filter shipment, a water cooling condenser was used for most of the experimental runs

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Schematic of mini-catalytic reactor

Temperature Controller

Pressure Transducer

Flow Meter

Computer

GC

Membrane or Condensor

Reaction Cell

Vacuum or Purge Gas

Heater

Magnetic Stir

Flow Meter

Nitrogen Gas

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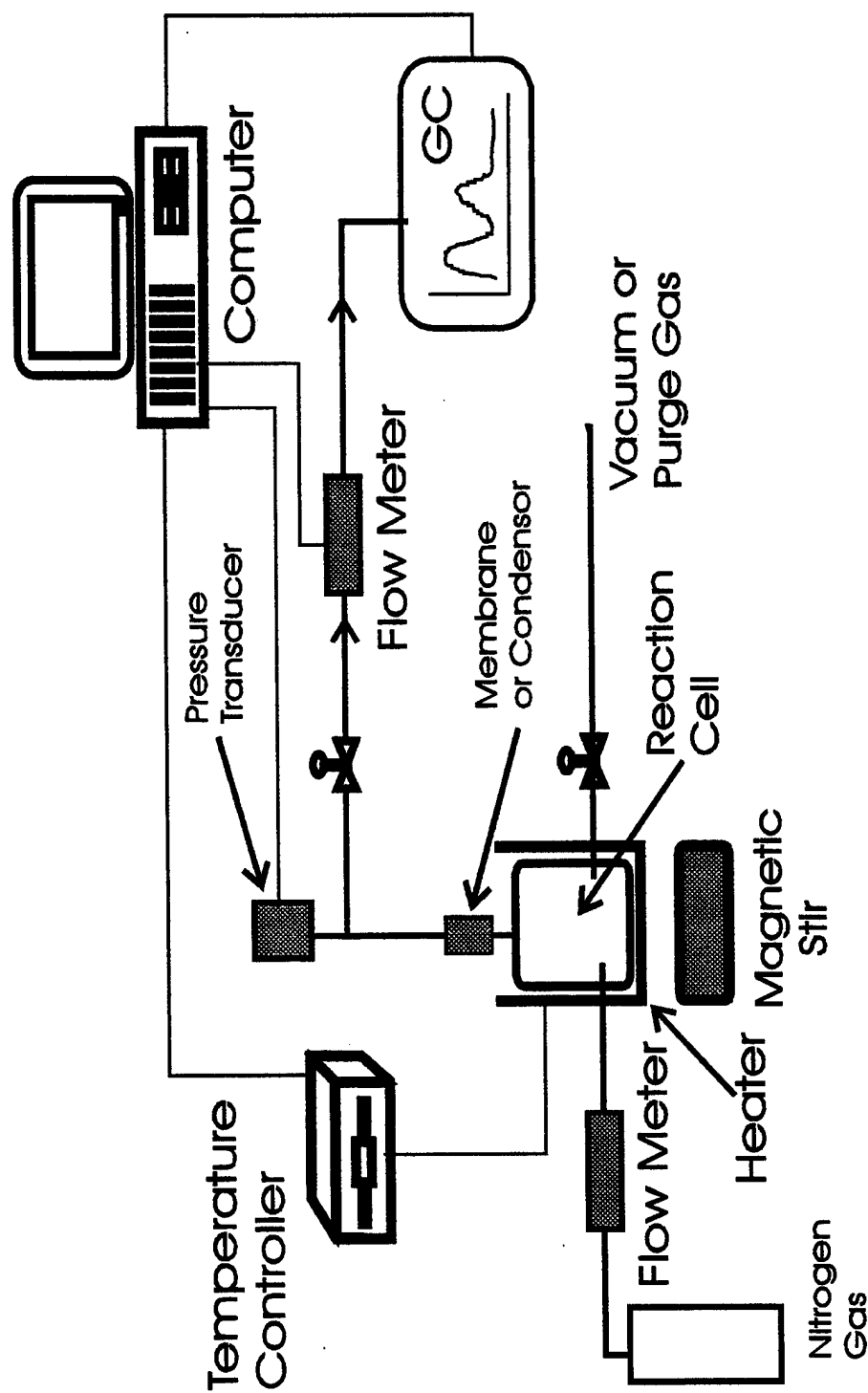
Experiment-Cont'd

- Proper selection of catalysts is crucial to achieve decalin dehydrogenation at lower temperature and achieve higher decalin-naphthalene conversion

- Although Ni and Pd based catalysts are also effective for decalin dehydrogenation, only Pt based catalysts can achieve over 65% decalin conversion within 3 hours at 260°C

Experiment-Cont'd

- The catalyst of 5% Pt on carbon support is effective for decalin dehydrogenation

- Typical dehydrogenation experimental run conditions:

  5% Pt on carbon support

  40 ml decalin, 0.5-1.0 gram catalyst,

  240-260°C, 3-5 hours

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Hydrogen Release

- With 260°C dehydrogenation temperature, about 18.5 liter hydrogen can be released from 40 ml decalin within 3 hours, or 64% decalin to naphthalene conversion. Over 77% conversion can be achieved within 5 hours

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Hydrogen release rate and cumulative amount-
with water cooling condenser

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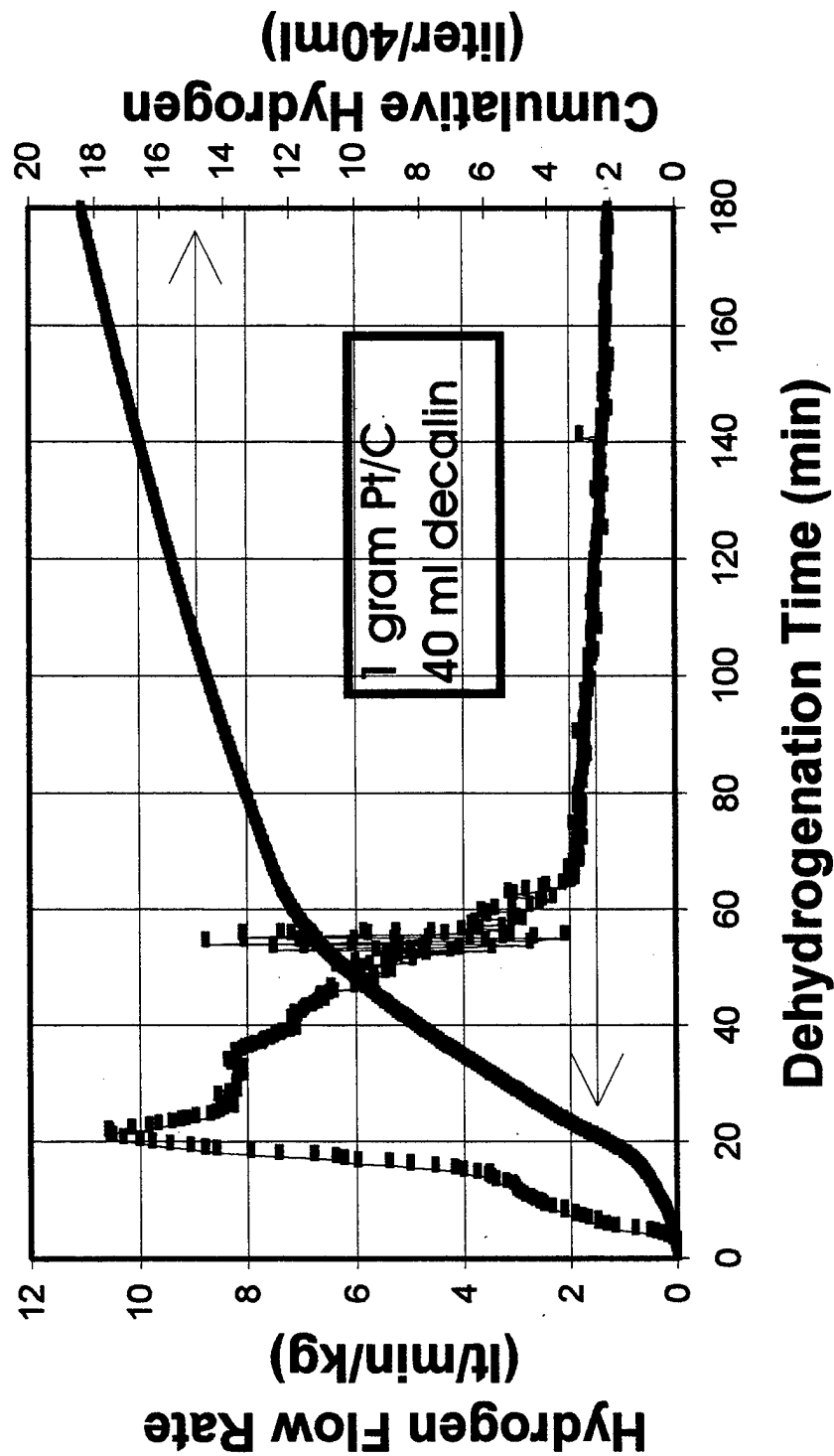
Hydrogen release rate and cumulative amount- with hydrogen membrane filter
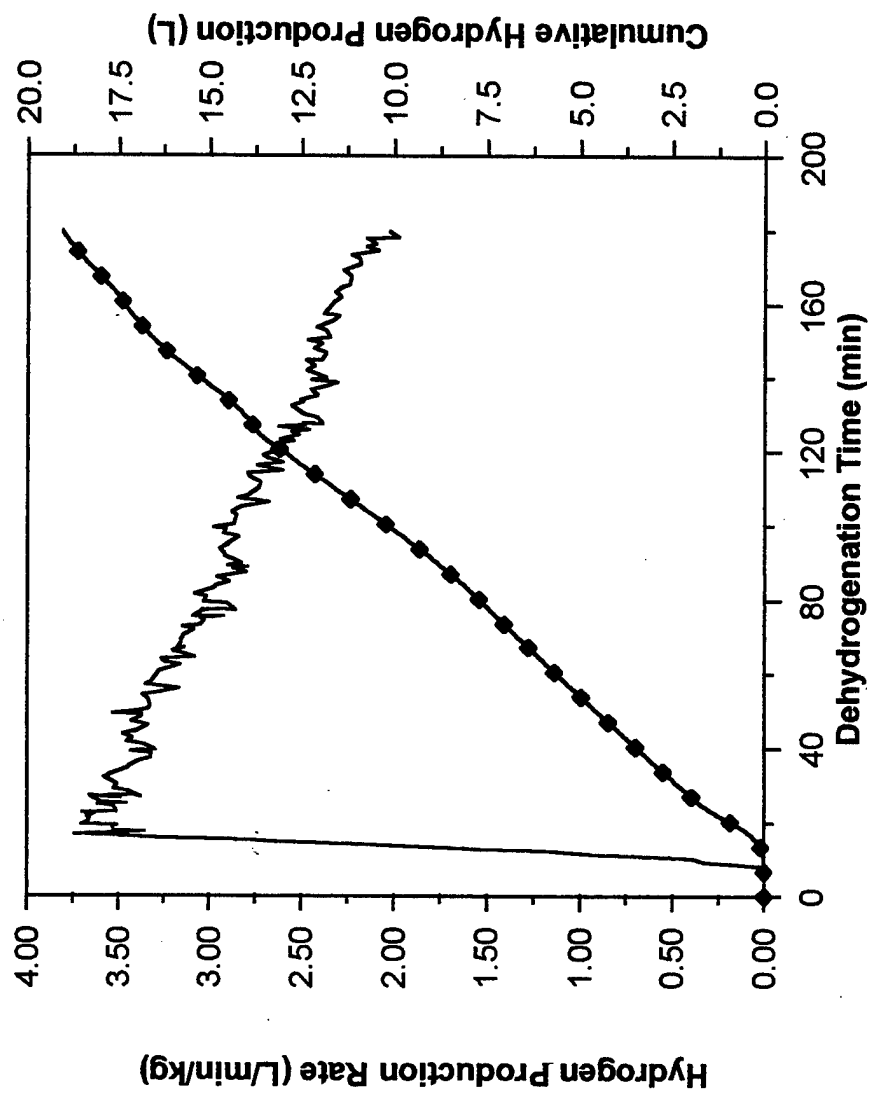
Hydrogen Release-Cont'd

- Hydrogen release from decalin strongly depends on the dehydrogenation temperature

- Hydrogen release flow rate can be regulated without significant effect on the process

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Hydrogen release versus temperature

5% Pt on carbon

260°C

250°C

240°C

Hydrogen Production (liter)

Dehydrogenation Time (min)

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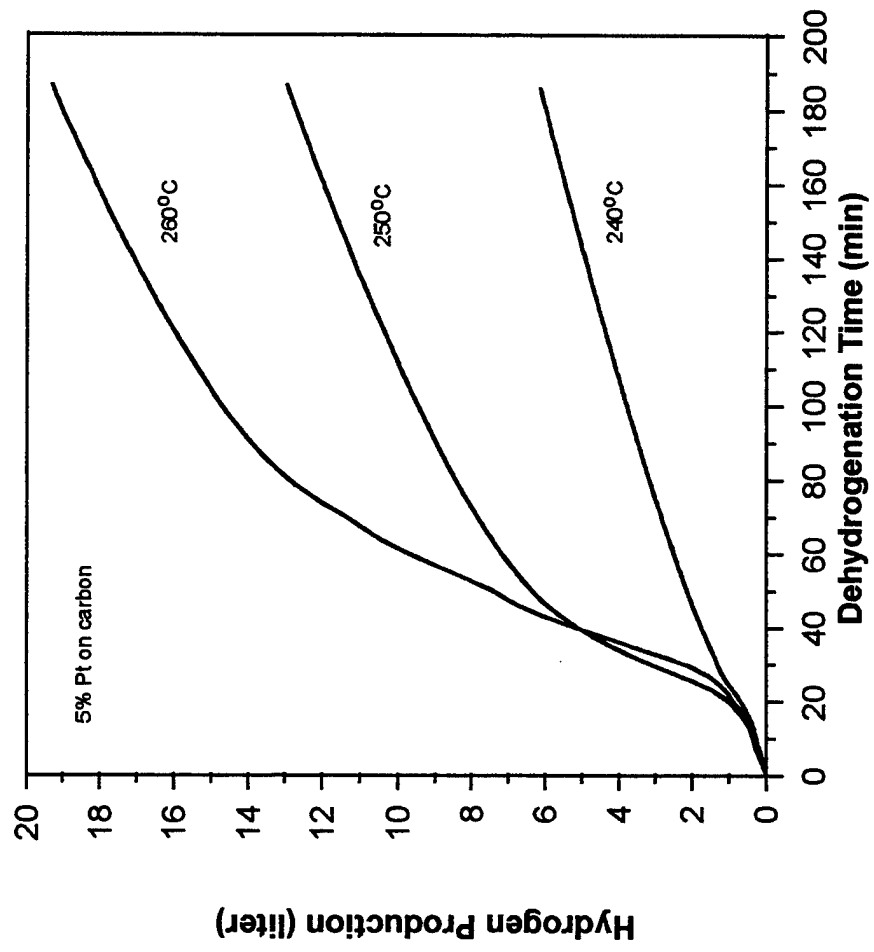
Hydrogen release with restricted flow rate
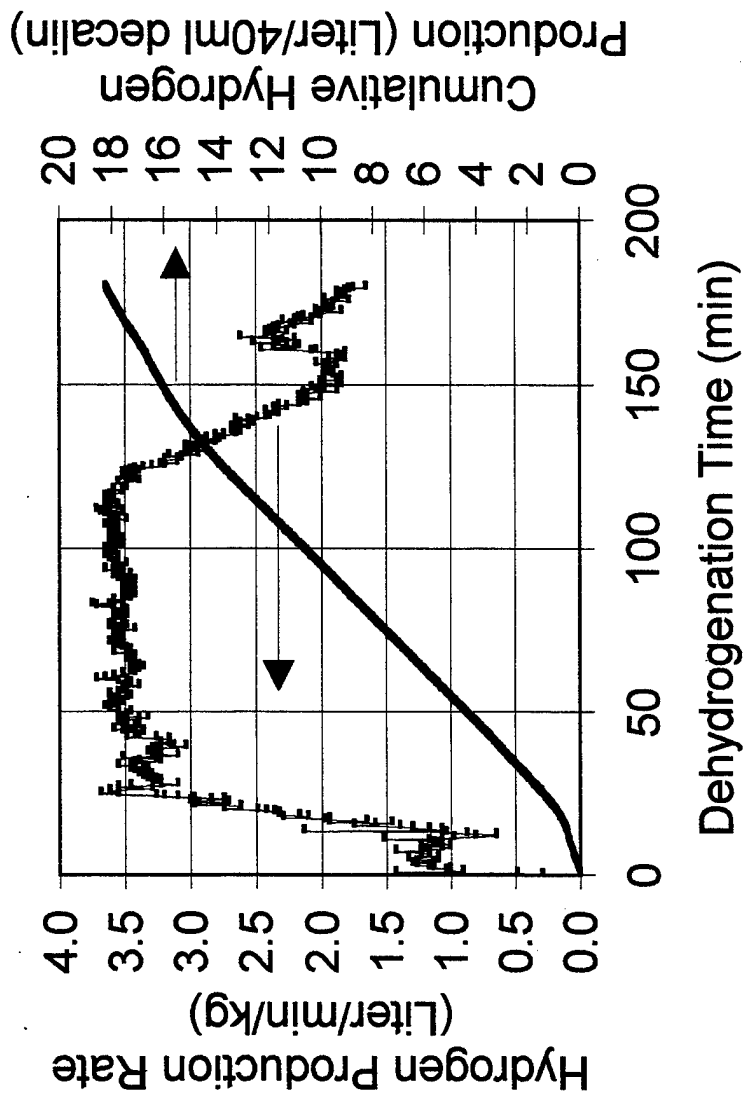
---------Orlando Meeting, MER Corporation---------

Hydrogen Charge-Release Cycles

- Decalin can be reversibly dehydrogenated and hydrogenated

- Hydrogenation experiment was carried out after decalin dehydrogenation using the same mini-reactor

- The hydrogenation was carried out at 180C with 10 atm hydrogen pressure

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Hydrogen Charge-Release Cycles-Cont'd

- 11 dehydrogenation-hydrogenation cycles have been performed so far, no significant performance deterioration was observed

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Dehydrogenation cycles

Cumulative Hydrogen Production (L) vs. Dehydrogenation Time (min)

Legend:
- + Cycle No. 1
- ◇ Cycle No. 5
- △ Cycle No. 10

Hydrogenation cycles

Cumulative Hydrogen Input (L) vs **Hydrogenation Time (min)**

Cycle No. 1 ✕
Cycle No. 5 ◇
Cycle No. 10 △

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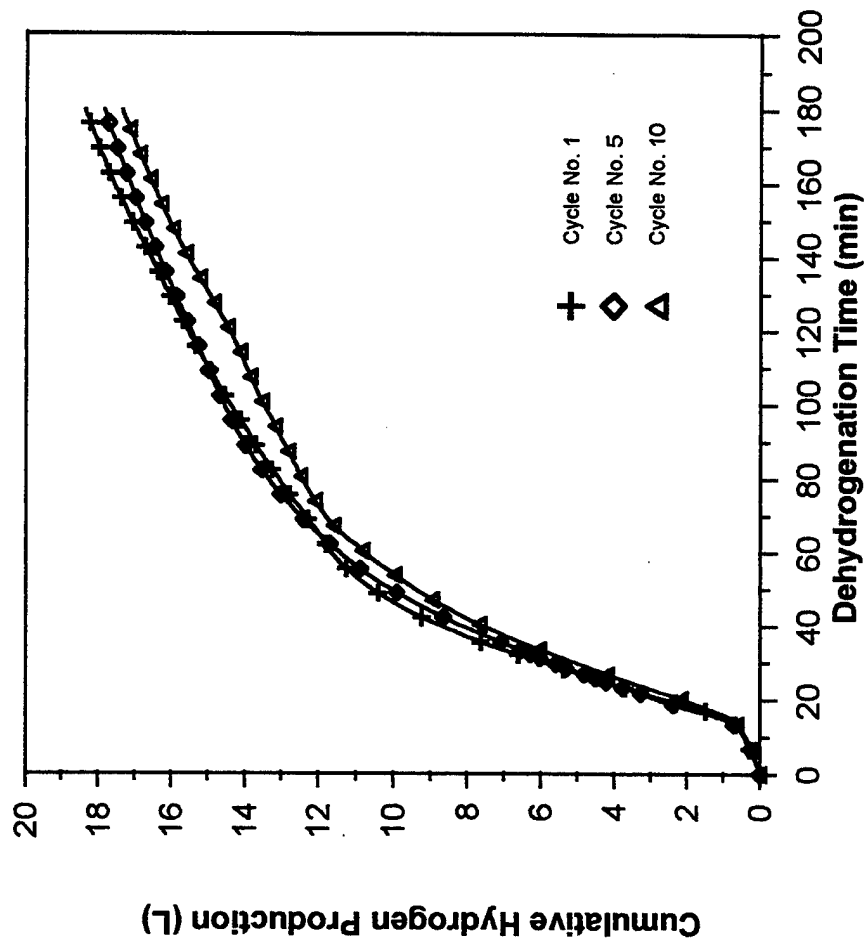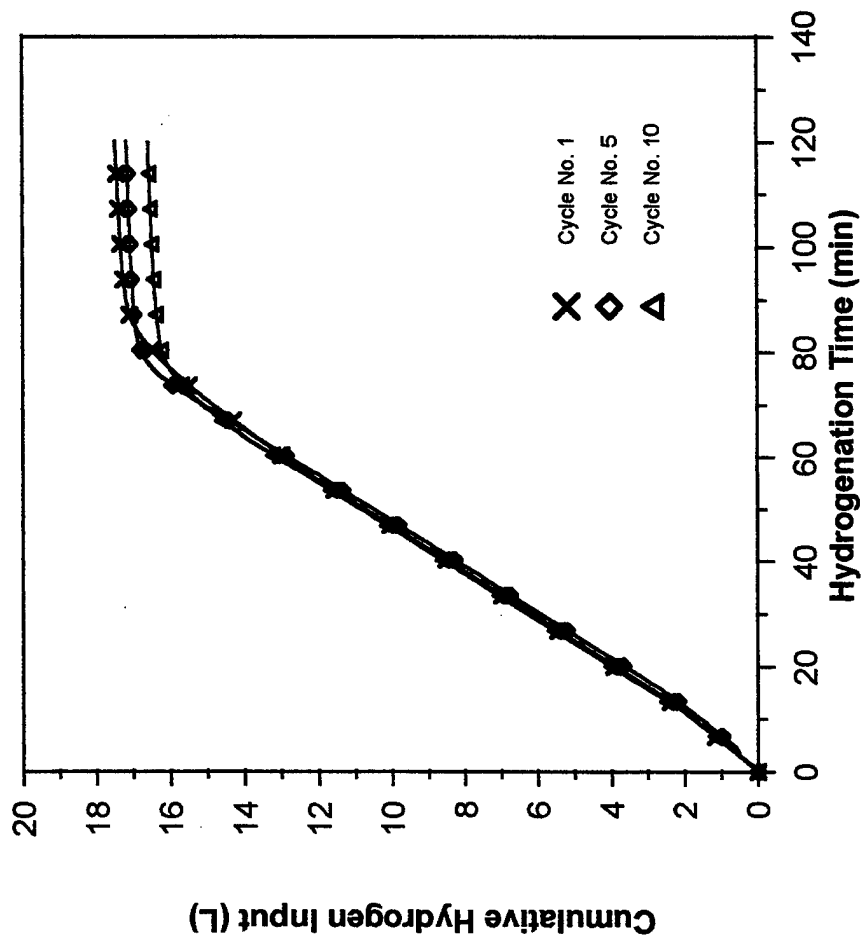
Energy Balance and System Specifications

- Hydrogen release is an endothermic process, for each mole of hydrogen release, $\Delta H_f/5$ energy is required

- Ea(De-Hy) was estimated from experimental results

194
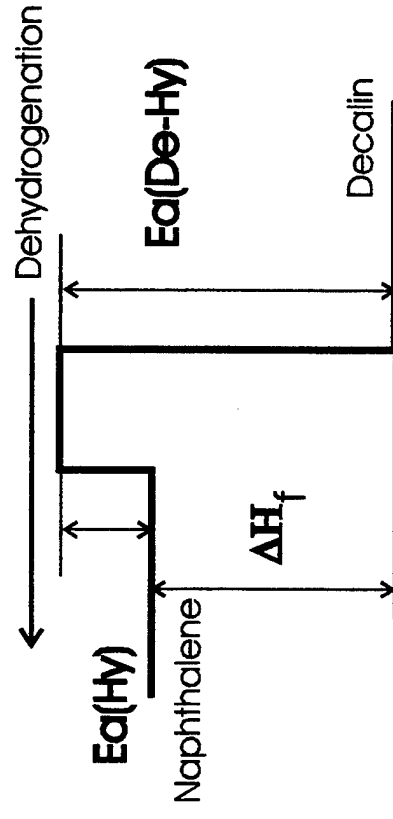
Energy Balance and System Specifications- Cont'd

- Ea(De-Hy) from experiments is 28.3 kJ/mole hydrogen, therefore, to release one mole hydrogen gas from decalin, less than 28.3 kJ energy is required

- This energy is equivalent to 9.96% of higher heating valve (HHV) of hydrogen gas

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Energy Balance and Specifications-Cont'd

gravimetric density	7.25%
volumetric density	65 kg/m^3
Ah/kg	1,944
Wh/kg	1,361
Wh/L	1,211
thermal burden	<28.3 kJ/mole H$_2$

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Energy Balance and Specifications-Cont'd

Wt for a 300W,10kWh   7.35 kg

Vol. for a 300W,10kWh   8.26 liter

Wt for a 100W, 1kWh   0.735 kg

Vol. for a 100W,1kWh   0.826 liter

Wt for a 10W, 90kWh   66.15 kg

Vol. for a 10W, 90kWh   74.32 liter

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Conclusions

- Liquid-hydride decalin is feasible for high density hydrogen storage applications

- The gravimetric and volumetric densities of hydrogen on decalin are 7.25% and 65kg/m^3

- Hydrogen release can be achieved by using Pt based catalyst at 260C, while hydrogen charge can be achieved at 180C with 10 atm H$_2$ pressure

- The system is simple, recyclable and inexpensive

- More research work is needed before a practical system can be developed

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ANALYTIC POWER CORPORATION

HYDROGEN FOR FUEL CELLS UNDER 1 KW

APRIL 8, 1997

to

US ARMY CECOM
FT BELVOIR, VA

SOURCES & SCALING LAWS

FUEL SYSTEMS WEIGHT & COST DISTRIBUTION

PRESSURIZED GAS

CHEMICAL HYDRIDE

HYDRIDE GUN

DIGITAL REACTOR

HYDROLYSIS

AMMONIA

HYDROCARBON

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FUEL SPECIFIC WEIGHT AND COST
CURRENT RETAIL

SOURCE	WHR/LB	CENT/kWH	WHR/in3
γ Conversion = 40%			
H2 GAS	7565	2353	4.62
NaBH4/NH4C1	668	1873	23.79
Mg + 2H2o	282	17714	17.33
CaH2 + H2O	391	15596	26.82
METHANOL	660	379	18.87
DIESEL	469	34	14.63
NH3	1077	93	29.97
Propane	889	34	18.78
Butane	876	319	18.31
BA5590	70	34483	3.33

SCALING LAWS

FUEL CELL WEIGHT =   A+B*POWER

H2 SOURCE WEIGHT =   (C+D*TIME)* POWER

SYSTEM WEIGHT=   A+(B+C+D*TIME)*POWER

SYSTEM COST =   A'+(B'+C'+D'*TIME)*POWER

Soldier Power System
Weight & Cost Scaling

Air Cooled Type 5.1 Systems
Analytic Power Corp

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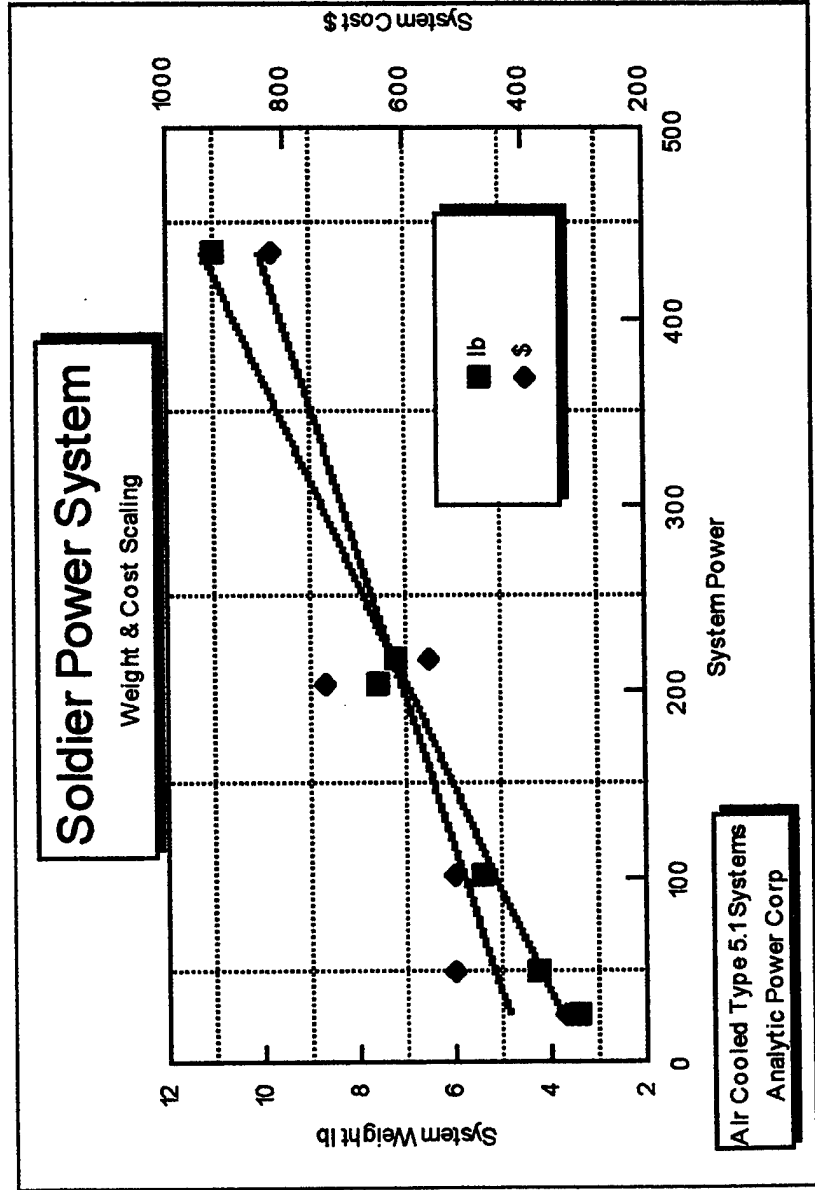
FUEL SYSTEM SCALING LAWS	WEIGHT		POWER	
	lb/kW	lb/kWH	$/kW	$/kWH
Hydrogen	9.52	6.00	$4,033	$1,100
Hydrides				
Hydrolysis	44.56	2.55	$1,309	$27
Digital Reactor	10.89	2.66	$4,521	$188
Hydride Gun	40.59	1.49	$11,964	$136
Ammonia	12.80	1.35	$570	$5
Butane	51.79	1.32	$2,925	$1

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Ratio Fuel Cell Power System to Battery Weight
Function of Power Level & Time

Power System Wt/Battery Wt

Legend:
- ■ 1
- ◆ 5
- ▲ 20
- ⊟ 50
- ◇ 100
- △ 200

Power Watts

Hydrogen
Air Cooled Type 5.1 Power System

Ratio Fuel Cell Power System to Battery Cost
Function of Power Level & Time

Power System $/Battery $

Legend:
- ■ 1
- ◆ 5
- ▲ 20
- ⊟ 50
- ◇ 100
- △ 200

Power Watts

Hydrogen
Air Cooled Type 5.1 Power System

204

Ratio Fuel Cell Power System to Battery Weight

Function of Power Level & Time

Power System Wt/Battery Wt vs Power Watts

Legend:
- 1
- 5
- 20
- 50
- 100
- 200

Ammonia Fuel
Air Cooled Type 5.1 Power System

Ratio Fuel Cell Power System to Battery Cost

Function of Power Level & Time

Power System $/Battery $ vs Power Watts

Legend:
- 1
- 5
- 20
- 50
- 100
- 200

Ammonia Fuel
Air Cooled Type 5.1 Power System

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Ratio Fuel Cell Power System to Battery Weight
Function of Power Level & Time

Power System Wt/Battery Wt

Legend:
- ■ 1
- ◆ 5
- ▲ 20
- ⊟ 50
- ◇ 100
- △ 200

Power Watts

Butane Fuel
Air Cooled Type 5.1 Power System

Ratio Fuel Cell Power System to Battery Cost
Function of Power Level & Time

Power System $/Battery $

Legend:
- ■ 1
- ◆ 5
- ▲ 20
- ⊟ 50
- ◇ 100
- △ 200

Power Watts

Butane Fuel
Air Cooled Type 5.1 Power System

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Ratio Fuel Cell Power System to Battery Weight
Function of Power Level & Time

Power System Wt/Battery Wt

Legend:
- 1
- 5
- 20
- 50
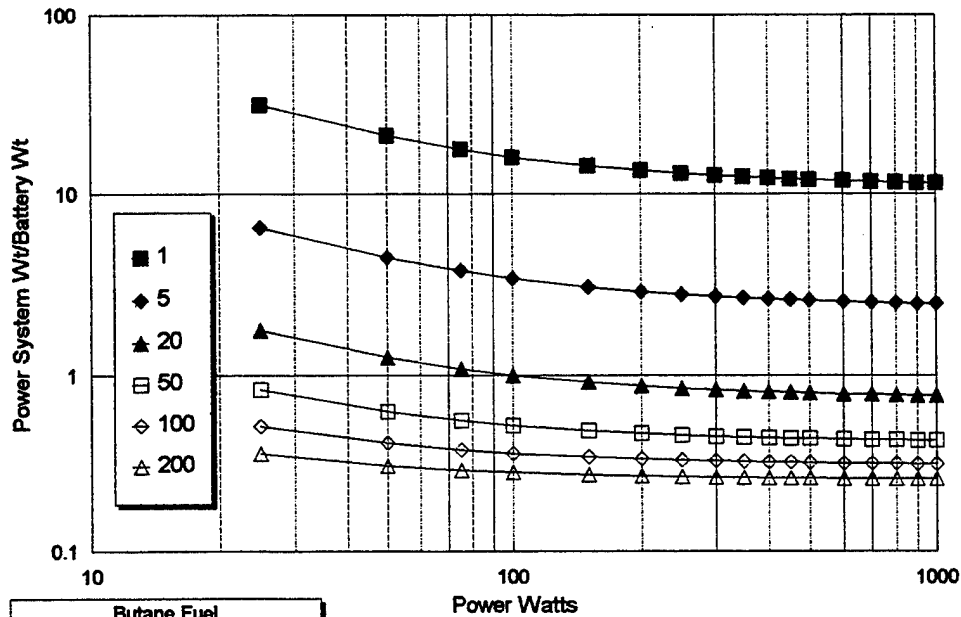- 100
- 200

Power Watts

Hydride Gun
Air Cooled Type 5.1 Power System

Ratio Fuel Cell Power System to Battery Cost
Function of Power Level & Time

Power System $/Battery $

Legend:
- 1
- 5
- 20
- 50
- 100
- 200
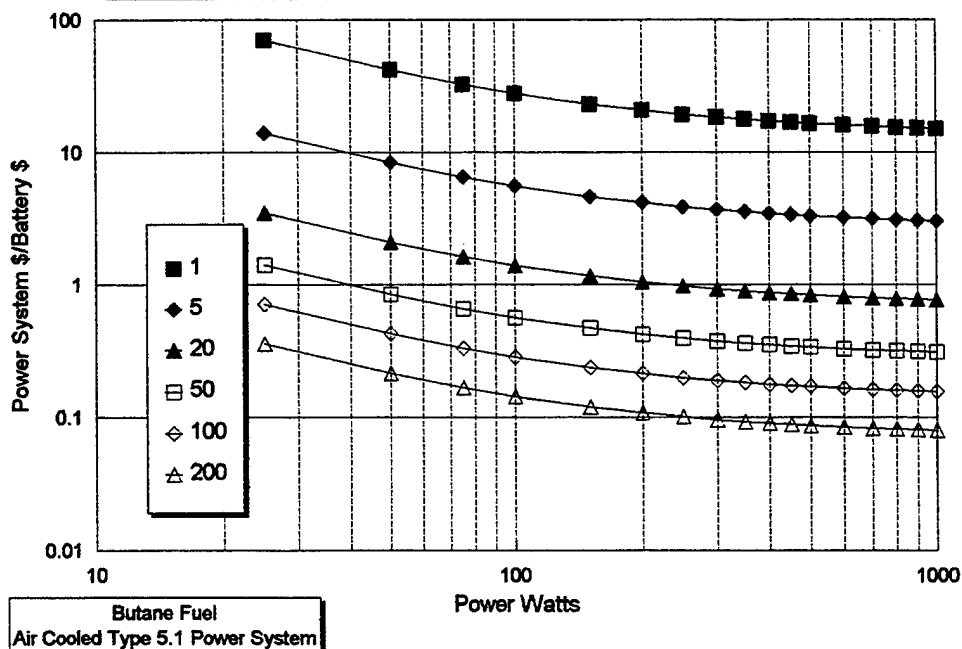
Power Watts

Hydride Gun
Air Cooled Type 5.1 Power System

207

Ratio Fuel Cell Power System to Battery Weight

Function of Power Level & Time

Power System Wt/Battery Wt

Power Watts

Legend:
- 1
- 5
- 20
- 50
- 100
- 200

Digital Reactor
Air Cooled Type 5.1 Power System
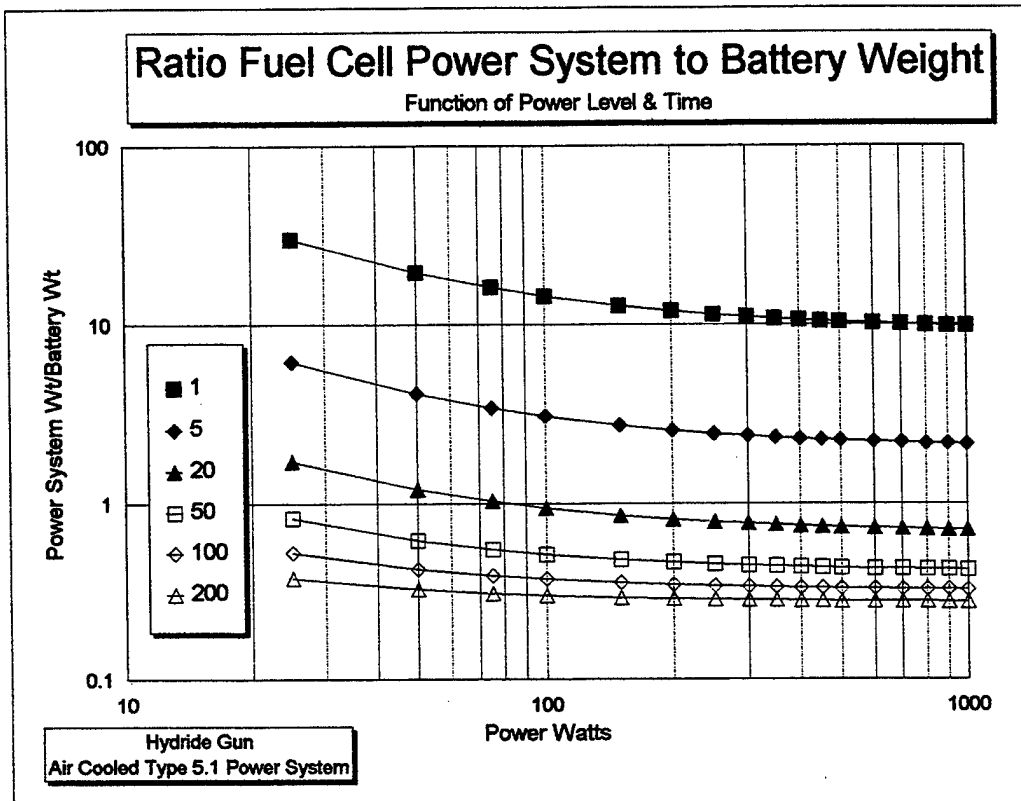
Ratio Fuel Cell Power System to Battery Cost

Function of Power Level & Time

Power System $/Battery $

Power Watts

Legend:
- 1
- 5
- 20
- 50
- 100
- 200

Digital Reactor
Air Cooled Type 5.1 Power System

208

C072 Hydrogen Source
250 whr   3000 psi

Component	Cost		Weight	
	$	%	lb	%
Tank	$275.00	31.3%	1.50	51.2%
Adaptor	$108.00	12.3%	0.19	6.4%
Valve	$59.00	6.7%	0.25	8.5%
Elbows	$15.00	1.7%	0.09	3.0%
Regulator	$185.00	21.0%	0.31	10.7%
CGA Ftg.	$27.00	3.1%	0.19	6.4%
Gauge	$15.00	1.7%	0.05	1.8%
Burst Disk	$176.00	20.0%	0.04	1.2%
CGA Caps	$20.00	2.3%	0.31	10.7%
	$880.00		2.93	

750 whr Supply

Component	Cost		Weight	
	$	%	lb	%
Tank 561	$320.00	35.2%	3.50	60.4%
Tank Fitting	$60.00	6.6%	0.25	4.3%
On/Off Valve el	$83.70	9.2%	0.33	5.7%
CGA Adaptor & N	$135.00	14.9%	0.59	10.2%
Regulator	$125.00	13.8%	0.50	8.6%
Burst Disk	$169.79	18.7%	0.57	9.8%
guage	$14.91	1.6%	0.05	0.9%
	$908.40		5.79	

Ammonia Cracker Fuel Cell Power Plant

210
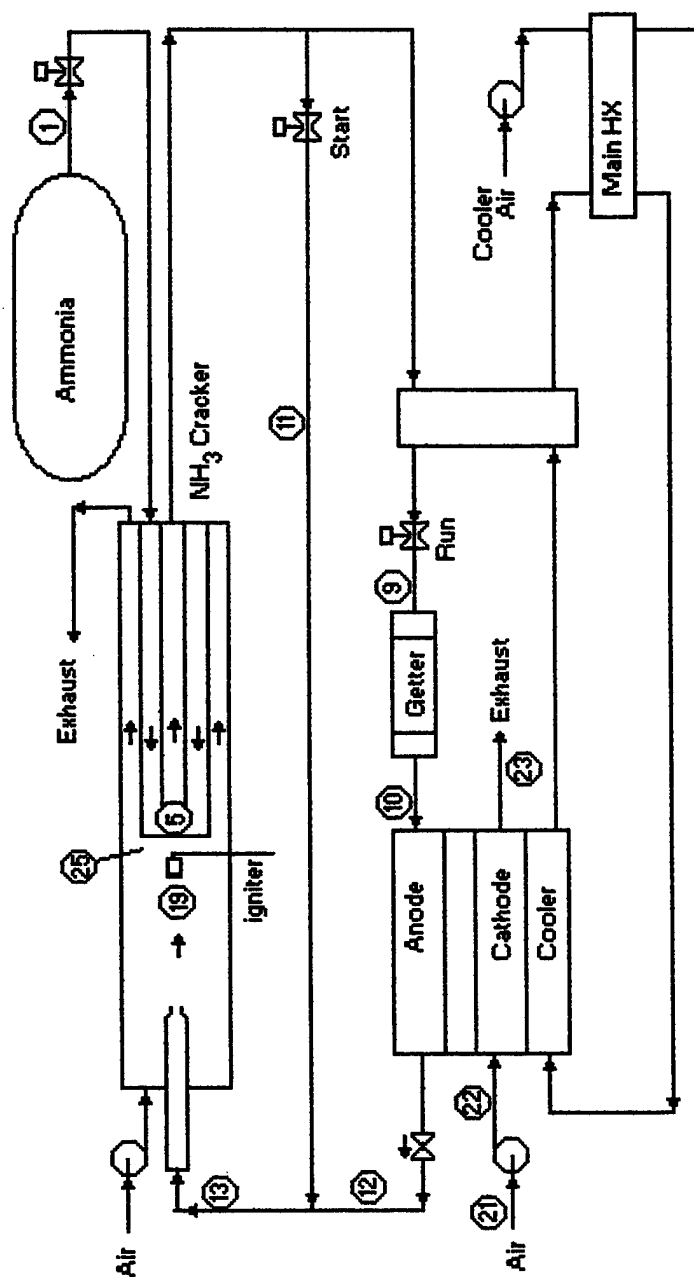
Soldier Power System 500 watt NH3

Component Cost Breakdown

COST- $

| 0.1 | 1 | 10 | 100 |

Package

Cracker

Burner Inlet Pump

Solenoid Valve Run

Solenoid Valve Start

Pressure Trans. (Ametek)

Female Quick Disconnect

Male Quick Disconnects

Pressure relief valve

Regulator#1 (Wilkerson)

NH3 Tank

Shell Caps (Ammonia)

Anode Inlet

Black P.P. 1/8"fnpt x 1/4" tube

Ammonia

Getter

Al Tee Fitting 1/8" FNPT

Al Tee Fitting 1/4" FNPT

Tubing Teflon PFA   1 Ft.

Black P.P. 1/8"mnpt x 1/4" tube

Black P.P. Tee

P.E. Adapter 1/8"mnpt X 1/4" mnpt

P.E. Fitting To Barb

LABOR

Components

211

Soldier Power System 500 watt NH3

Component Weight Breakdown

Weight - lb

Components			
0.01	0.1	1	10

Ammonia

Cracker

NH3 Tank

Package

Regulator#1 (Wilkerson)

Al Tee Fitting 1/4" FNPT

Anode Inlet

Shell Caps (Ammonia)

Pressure Trans. (Ametek)

Burner Inlet Pump

Female Quick Disconnect

Solenoid Valve Start

Solenoid Valve Run

Male Quick Disconnects

Al Tee Fitting 1/8" FNPT

Getter

Pressure relief valve

Tubing Teflon PFA   1 Ft.

Black P.P. 1/8"fnpt x 1/4" tube

Black P.P. 1/8"mnpt x 1/4" tube

Tubing vinyl 1 Ft.

Black P.P. Tee

212
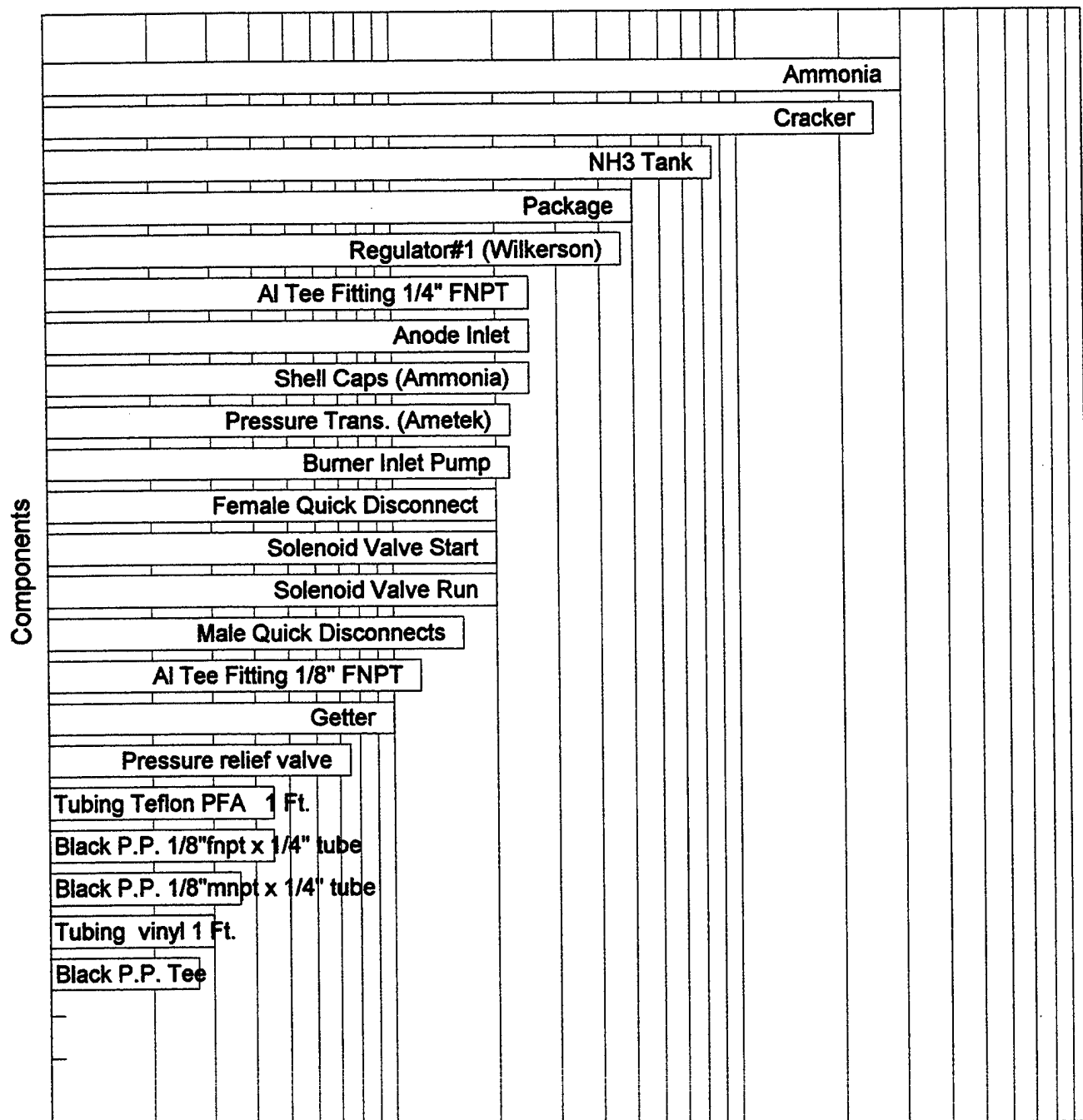
Concept

Chemistry

Beckert/Dengel reaction:

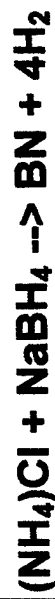m/n $(NH_4)_nX + Y(ZH_4)_m \rightarrow YX_{m/n} + mZN + 4mH_2$
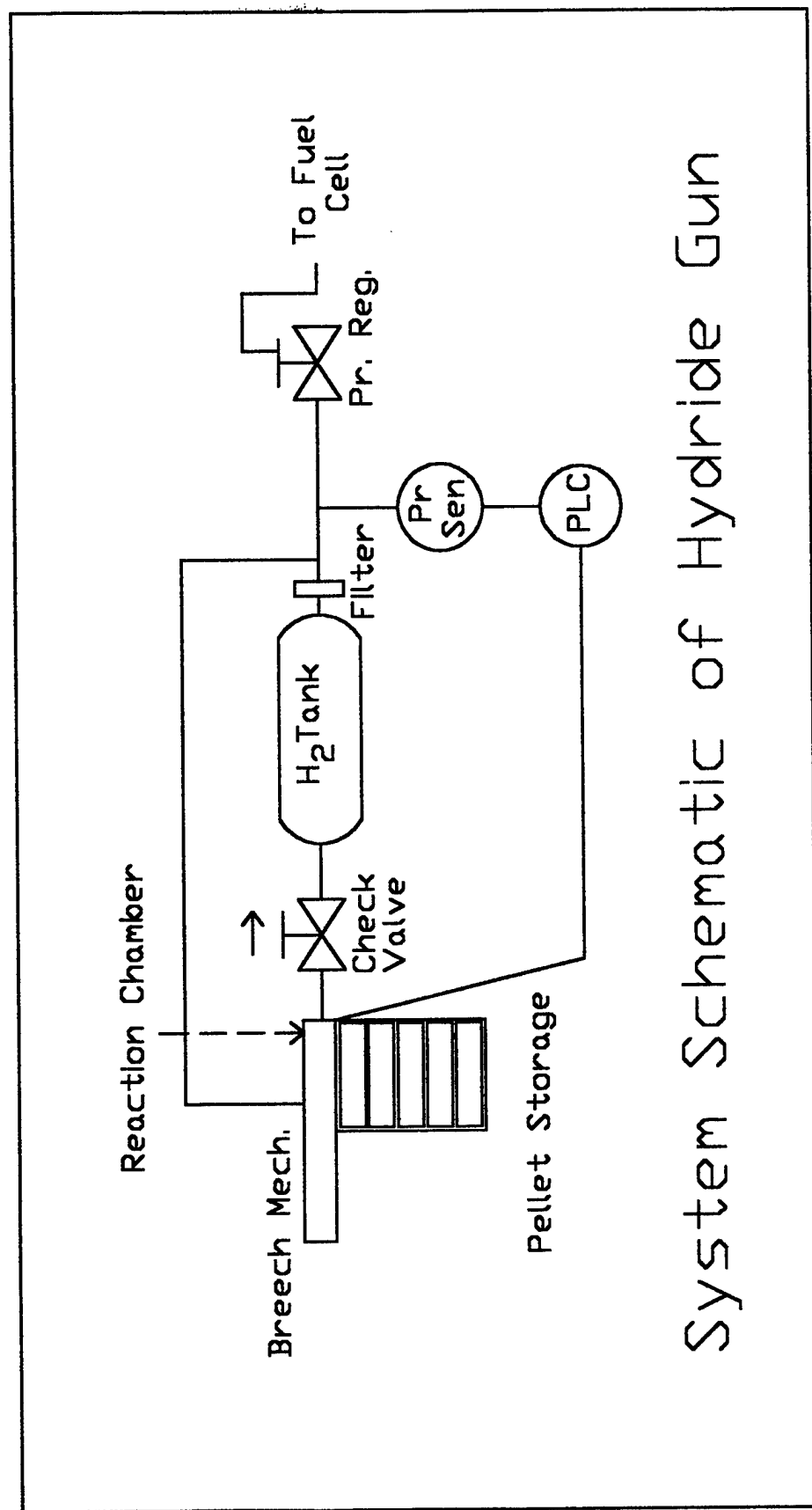
where: X inorganic anion

Y is an alkaline or alkaline earth metal

Z is a trivalent metal forming complex hydrides : Al or B.

m valence of Z and n valence of X

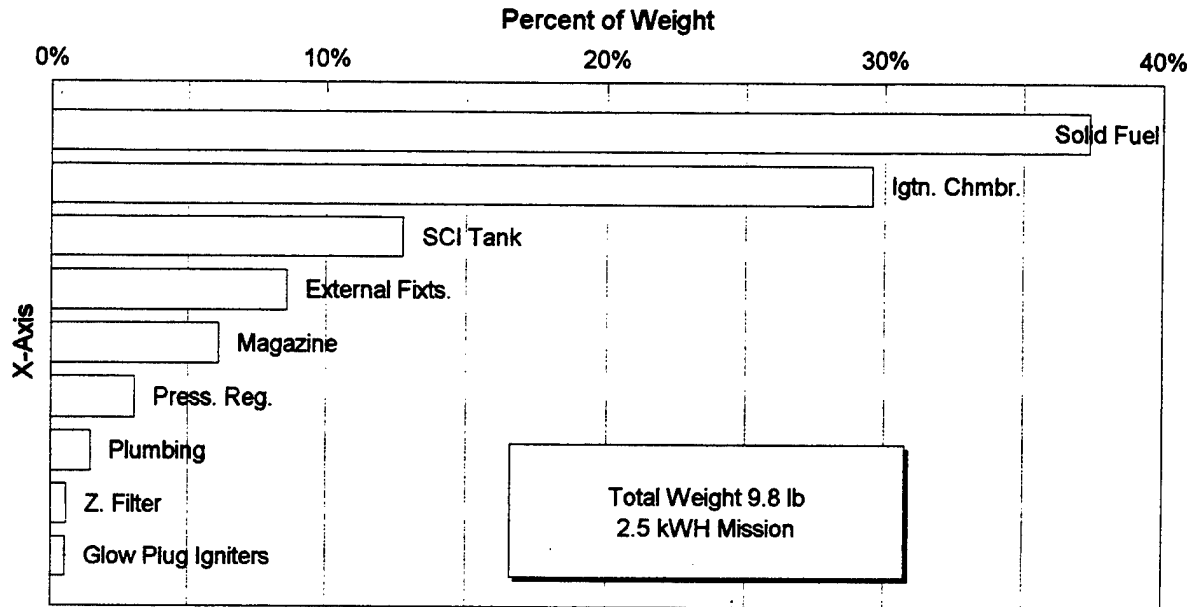Example let X be chlorine, Y be sodium and Z be boron.

$(NH_4)Cl + NaBH_4 \rightarrow BN + 4H_2$

System Schematic of Hydride Gun

214

Hydride Gun	Volume	Weight	Cost	
Pellet Type	Recipe 2			
50 cal				
Diam	1 in			
Length	4 in			
77.41 whr	3.14 in3	51.49 gm	$10.48	$135.39
	51.49 cm3			
	46.45 liter H2	1.00 gm/cc		
Capacity				
Total	3.14 in3	51.49 gm	$10.48	$135.39
MISSION	2.5 kWH			
Pellets	32			
	129.18 in3	3.67 lb	$338.48	$135

Hydride Gun	weight		cost	
	lb	%	$	%
Solid Fuel	3.67	37.4%	$338	15.9%
Igtn. Chmbr.	2.90	29.6%	$300	14.1%
SCI Tank	1.25	12.7%	$275	12.9%
External Fixts.	0.84	8.6%	$639	29.9%
Magazine	0.60	6.1%	$100	4.7%
Press. Reg.	0.30	3.1%	$180	8.4%
Plumbing	0.14	1.4%	$300	14.1%
Z. Filter	0.06	0.6%	$1	0.0%
Glow Plug Igniters	0.05	0.5%	1	0.0%
Total	9.80		$2,134	
Tot. Wt. H2 (lb):	0.33			
Wt% H2:	3.37%			

Hydride Gun Weight Breakdown
Analytic Power Corp.

Percent of Weight

0%	10%	20%	30%	40%

- Solid Fuel
- Igtn. Chmbr.
- SCI Tank
- External Fixts.
- Magazine
- Press. Reg.
- Plumbing
- Z. Filter
- Glow Plug Igniters

X-Axis

Total Weight 9.8 lb
2.5 kWH Mission

Hydride Gun Cost Breakdown
Analytic Power Corp.

Percent Cost

0%	10%	20%	30%	40%

- Solid Fuel
- Igtn. Chmbr.
- SCI Tank
- External Fixts.
- Magazine
- Press. Reg.
- Plumbing
- Z. Filter
- Glow Plug Igniters

X-Axis

Total Cost $2,134
2.5 kWH Mission

216

LEXAN HOUSING

TRASH
AREA

Ø12"

217

CROSS SECTION THRU "ACTION"

218

LiAlH$_4$/NH$_4$Cl
Reaction Chamber

Slides

Chamber

Trigger

219

LiAlH$_4$/NH$_4$Cl Pellet Dispenser

Incoming Pellets

Rotator

Front View

Side View

220

Circuit Board

Pellets

Insulation

6.5000

6.5000

212

223

Fuel Box Weight Distribution

2500 WHR Fuel Box

weight lb

0.0001	0.001	0.01	0.1	1	10

7 — reactor housing
2 — NH4Cl
1 — LiAlH4
11 — insulation
8 — circuit boards
9 — card extenders
4 — mineral oil
6 — pellet igniters
5 — Kraton thermoplastic rubber
13 — board relay
15 — pressure transducer
22 — pressure gauge
26 — female quick disconnect valve
21 — pressure transducer
29 — pellet counter display
14 — power source
20 — pressure control switch
27 — male quick disconnect valve
10 — card guides
24 — pressure relief valve
23 — pressure regulator
25 — teflon tubing
12 — board connectors
16 — on/off switch
28 — external cable
17 — on/off indicator (green)
19 — auto shutoff indicator (red)
18 — fuel low indicator (yellow)
3 —

Weight Total 12 lb

224

Fuel Box Cost Distribution

2500 whr

Cost $

	1	10	100	1000

1 — LiAlH4

29 — pellet counter display

6 — pellet igniters

2 — NH4Cl

9 — card extenders

8 — circuit boards

7 — reactor housing

20 — pressure control switch

11 — insulation

12 — board connectors

24 — pressure relief valve

15 — pressure transducer

21 — pressure transducer

16 — on/off switch

14 — power source

22 — pressure gauge

26 — female quick disconnect valve

27 — male quick disconnect valve

28 — external cable

5 — Kraton thermoplastic rubber

4 — mineral oil

3 — toluene

13 — board relay

18 — fuel low indicator (yellow)

17 — on/off indicator (green)

10 — card guides

19 — auto shutoff indicator (red)

25 — teflon tubing

23 —

Total Cost $2,273

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Control Schematic
Analytic Power Corp.
C070

SOLDIER POWER SYSTEM

Hydrolysis Reactor NaBH4 - H2O

Cost $1,205

Cost $

$0.0	$0.1	$1.0	$10.0	$100.0	$1,000.0

X-Axis

Shell Caps (Hydrogen Reactor)
Shell Cap (Water Supply)
SodiumBoroHydride
Solenoid Valve (Water)
Reactor Shell
Water Shell
Pressure Trans. (Ametek)
Bladder For Water Supply
Regulator #2 (Airtrol)
Pressure relief valve
Solenoid Valve (H2 Exit)
Female Quick Disconnect
Male Quick Disconnects
S.S. Tee Fitting 1/4" FNPT
S.S. Tee Fitting 1/8" FNPT
Regulator#1 (Wilkerson)
Valve for inlet
Porous Plastic Tubing(H2 Exit)
Black P.P. 1/8"fnpt x 1/4" tube
S.S. adapter 1/4" mnpt x 1/8" fnpt
Acetic Acid
Tubing Teflon PFA 1 Ft.
Black P.P. 1/8"mnpt x 1/4" tube
CO2 Container
Air Inlet Valve
Black P.P. Tee
P.E. Adapter 1/8"mnpt X 1/4" mnpt
P.E. Fitting To Barb.
Tubing vinyl 1 Ft.

Hydrolysis Reactor NaBH4 - H2O

Weight 9.25 lb

Weight lb

| 0.001 | 0.01 | 0.1 | 1 | 10 |

X-Axis

- Water
- SodiumBoroHydride
- Reactor Shell
- Water Shell
- Regulator#1 (Wilkerson)
- Acetic Acid
- S.S. Tee Fitting 1/4" FNPT
- Shell Cap (Water Supply)
- Shell Caps (Hydrogen Reactor)
- Pressure Trans. (Ametek)
- Female Quick Disconnect
- Solenoid Valve (Water)
- Bladder For Water Supply
- Porous Plastic Tubing(H2 Exit)
- Male Quick Disconnects
- S.S. Tee Fitting 1/8" FNPT
- CO2 Container
- Pressure relief valve
- Regulator #2 (Airtrol)
- S.S. adapter 1/4" mnpt x 1/8" fnpt
- Solenoid Valve (H2 Exit)
- Tubing Teflon PFA   1 Ft.
- Black P.P. 1/8"fnpt x 1/4" tube
- Valve for inlet
- Air Inlet Valve
- Black P.P. 1/8"mnpt x 1/4" tube
- Tubing vinyl 1 Ft.
- Black P.P. Tee
- P.E. Adapter 1/8"mnpt X 1/4" mnpt
- P.E. Fitting To Barb

Regenerative Autothermal Reforming (RAT)
Fuel Cell Power Plant

230
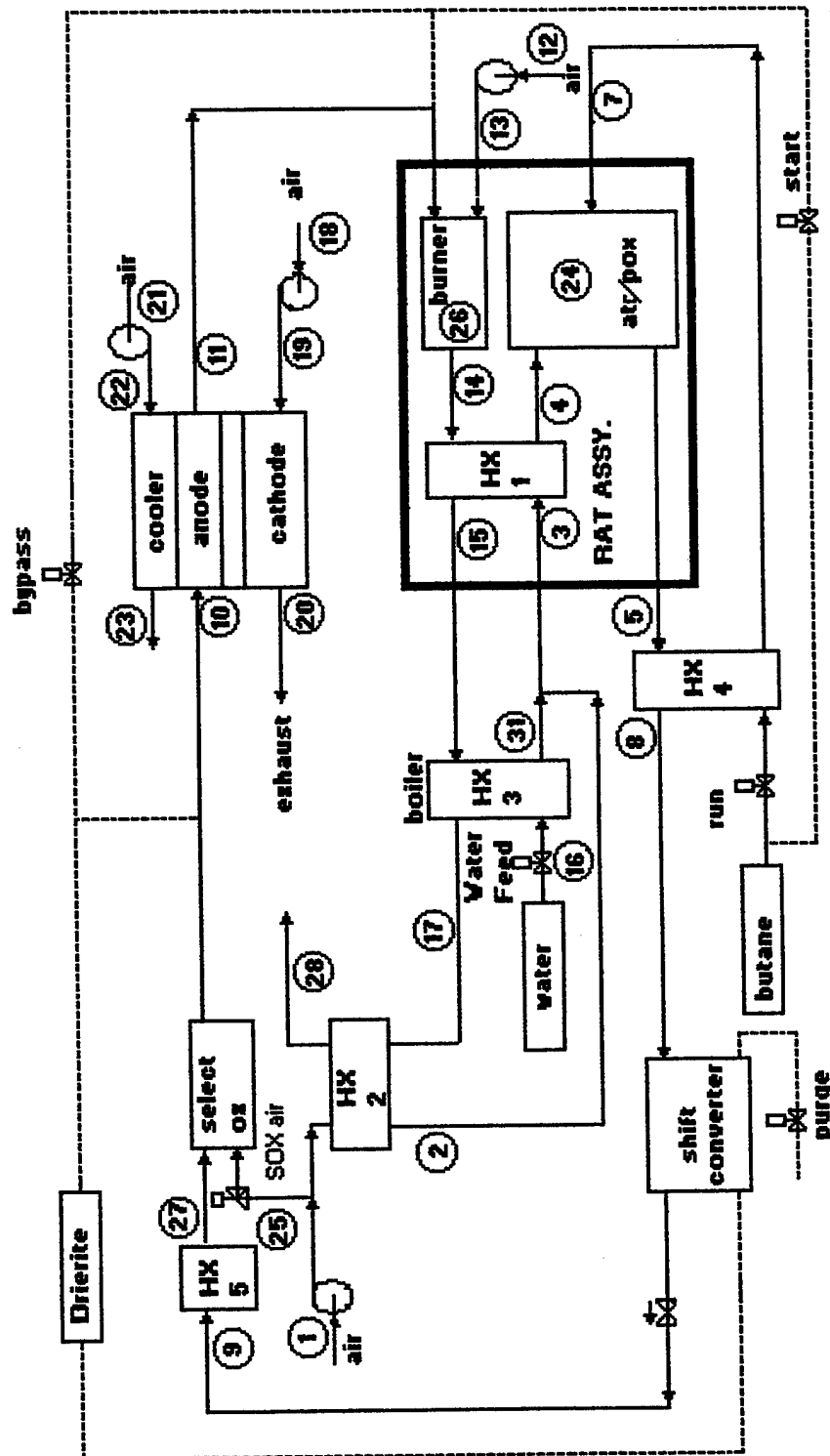
Compact Fuel Processors Based on Microsystem Technologies

Robert S. Wegeng

M. Kevin Drost

Battelle Memorial Institute
Pacific Northwest National Laboratory

Manportable Power Generation: Characteristics of an Ideal Solution

- Low weight

- Long duration

- Minimize impact on logistics

- Low thermal signature

Mesoscopic Power Cell

Liquid
Fuel Storage

Mesoscopic
Fuel
Processor

Mesoscopic
Fuel Cell

Lithium
Polymer
Battery
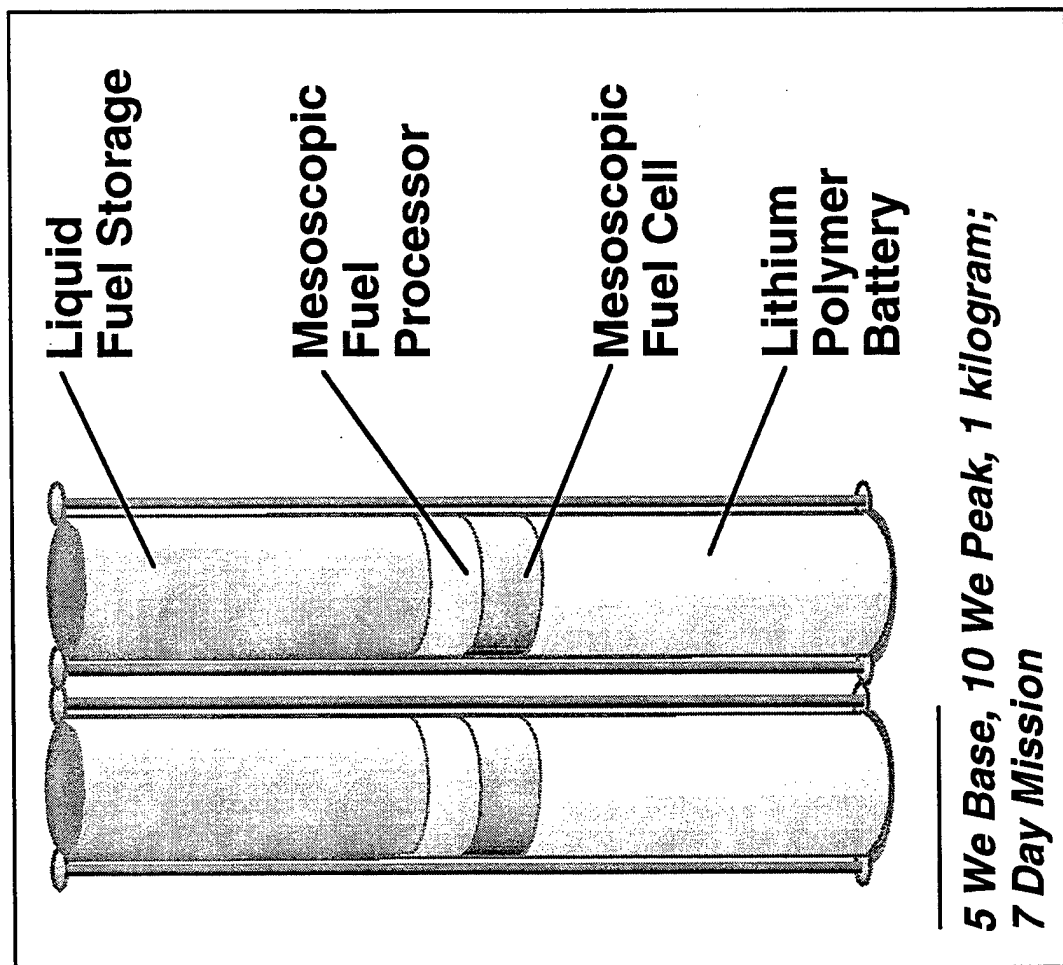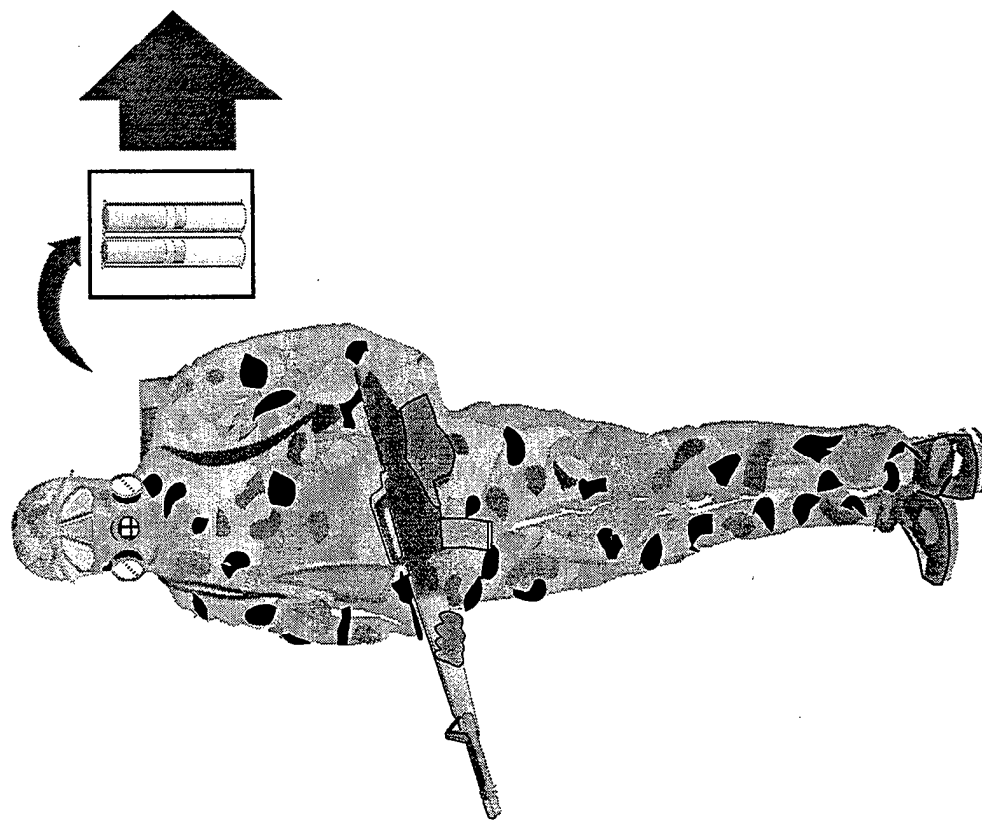
*5 We Base, 10 We Peak, 1 kilogram;
7 Day Mission*

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Outline

- Introduction

- Background

- Concept Details and
  Development Status

- Technical Challenges

- Summary

Why Microtechnology?

- **Size and weight:**
  Microstructures enable the utilization of
  - Enhanced heat transfer rates, and
  - Enhanced mass transport rates,
    thus providing *higher capacities* per unit volume/weight

- **Selectivity:**
  Improved product yields through precise control of process conditions

- **Cost:**
  Microfabrication techniques support mass production of integrated systems

Sizes/Characteristics of Microcomponents
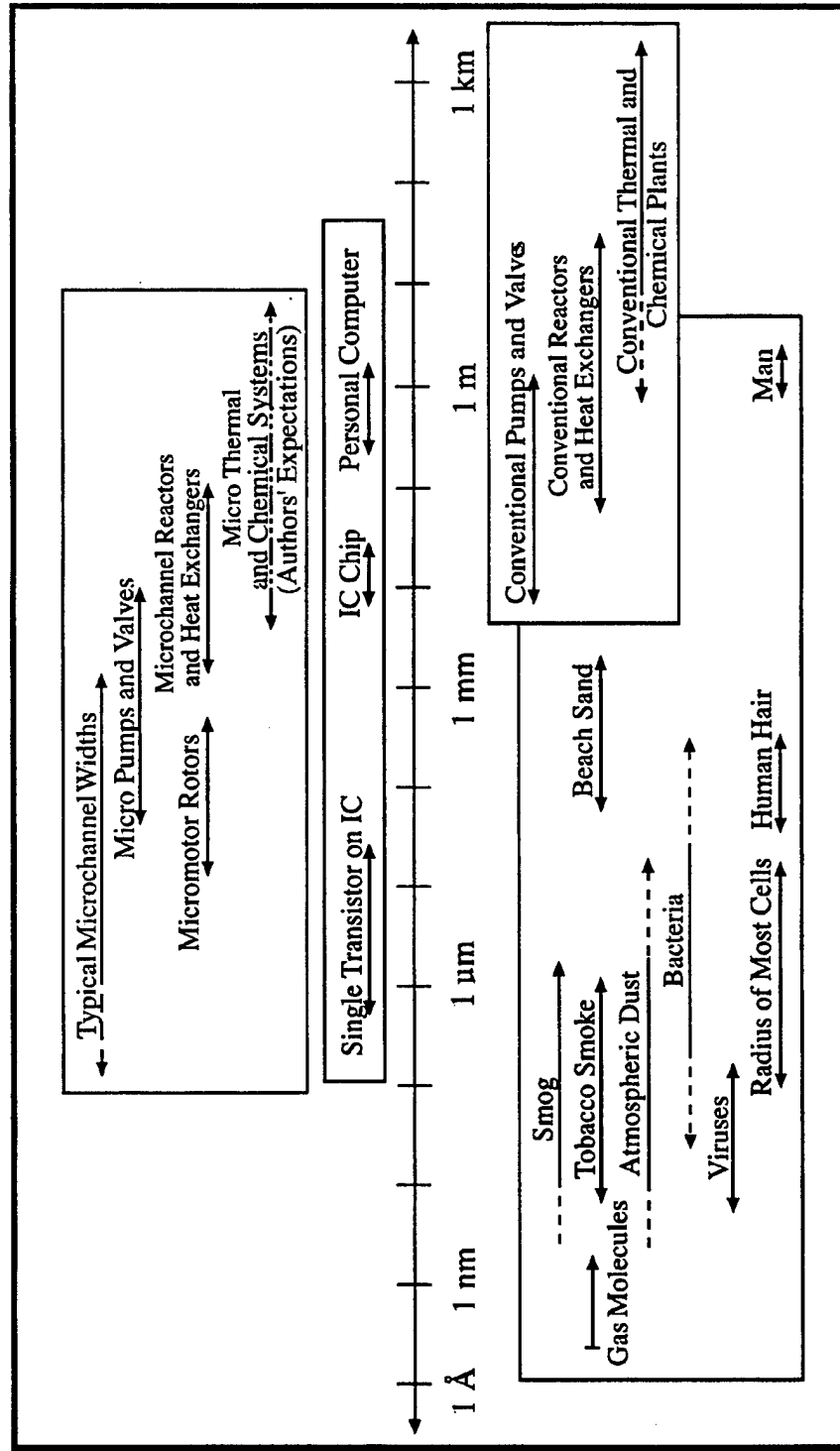
Europe: *Microsystems Technology and Microreaction Technology*
DARPA's Defense Science Office: *Mesoscopic Machines*

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Potential Paradigm Shift

An important paradigm shift that would occur with such mesoscopic systems is that the overall weight would now be dominated by fuel, rather than hardware.

This would have broad impact across a variety of DoD applications requiring electrical power or propulsion.

Observation attributed to Prof. Alan Epstein, MIT, in DARPA DSRC Report on Mesoscopic Machines

Heat and Mass Transport Advantages in Engineered Microchannels

RG97040024. 8

Performance
- 100 Wt per square centimeter
- High convective heat transfer coefficient
  - 13,000 - 15,000 Wt/m²-K (liquids)
  - 20,000 - 30,000 Wt/m²-K (boiling)
- Low pressure drops (1-2 psi)
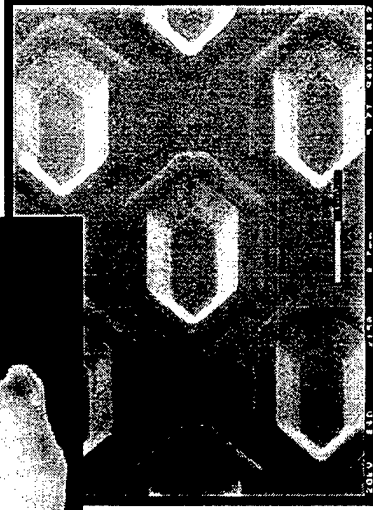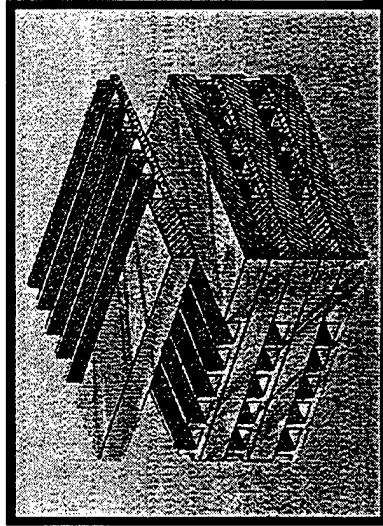
Performance
- 20 kWt per cubic centimeter

238

Heat and Mass Transport Advantages in Engineered Microchannels
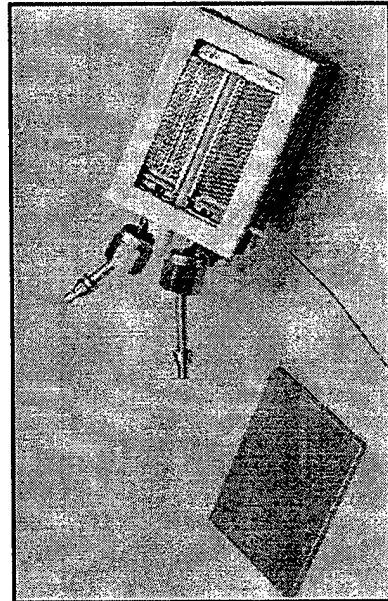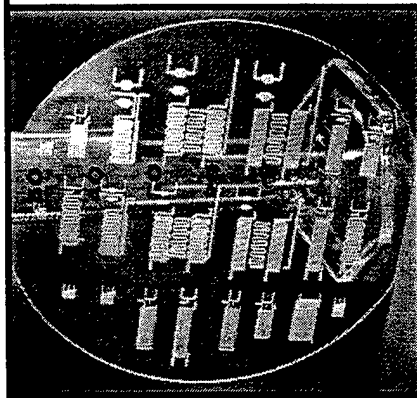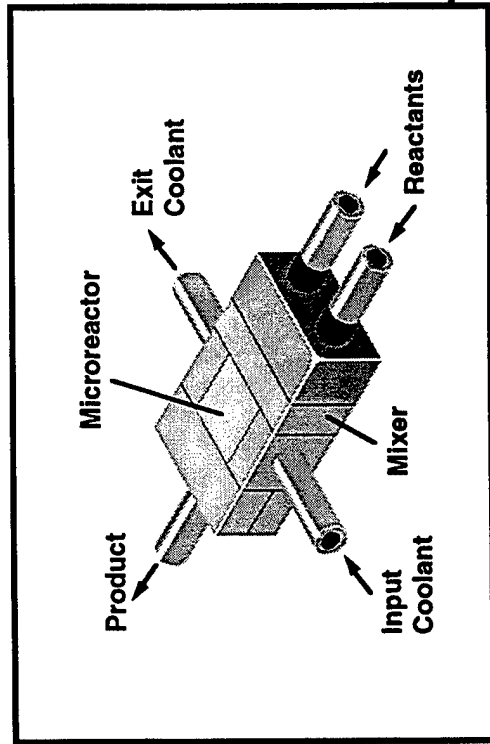
Performance
- 30 w/cm² heat transfer rate
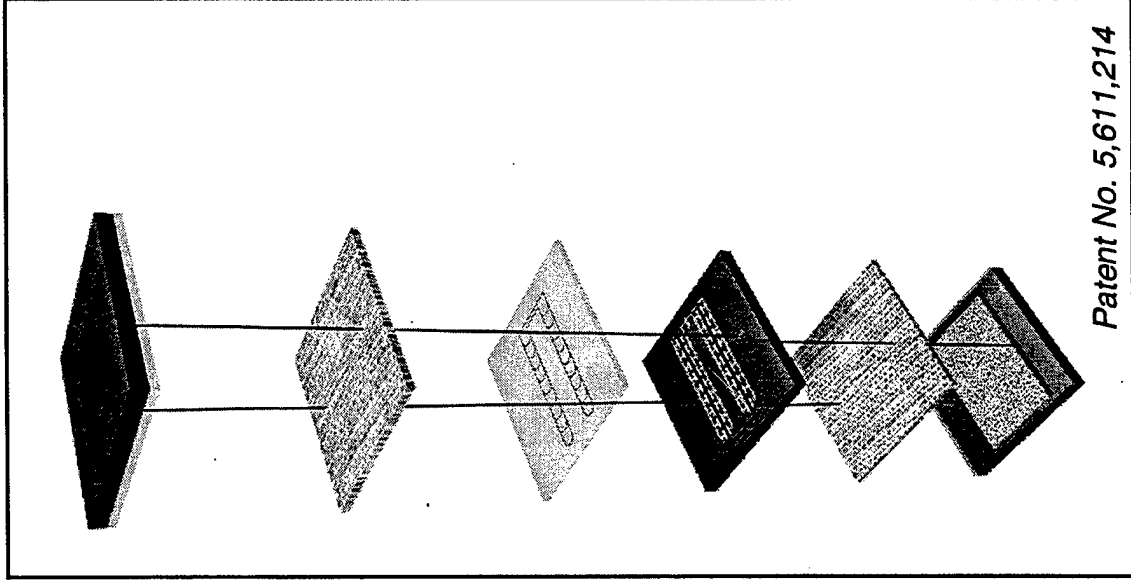- 85-93% efficiency
- Rapid thermal response (1 minute)

Water In

Steam Out

Products Out

Fuel + Oxygen In

Catalyst- Coated Microchannels

RG97040024. 9

Exit Coolant

Reactants

Microreactor

Product

Mixer

Input Coolant

239
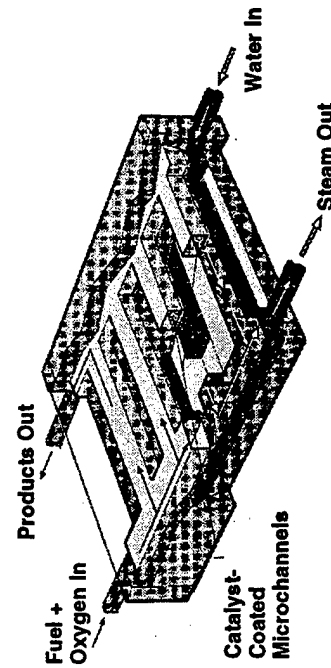
PNNL Microtechnology Program

- Develop micro components that can perform unit operations
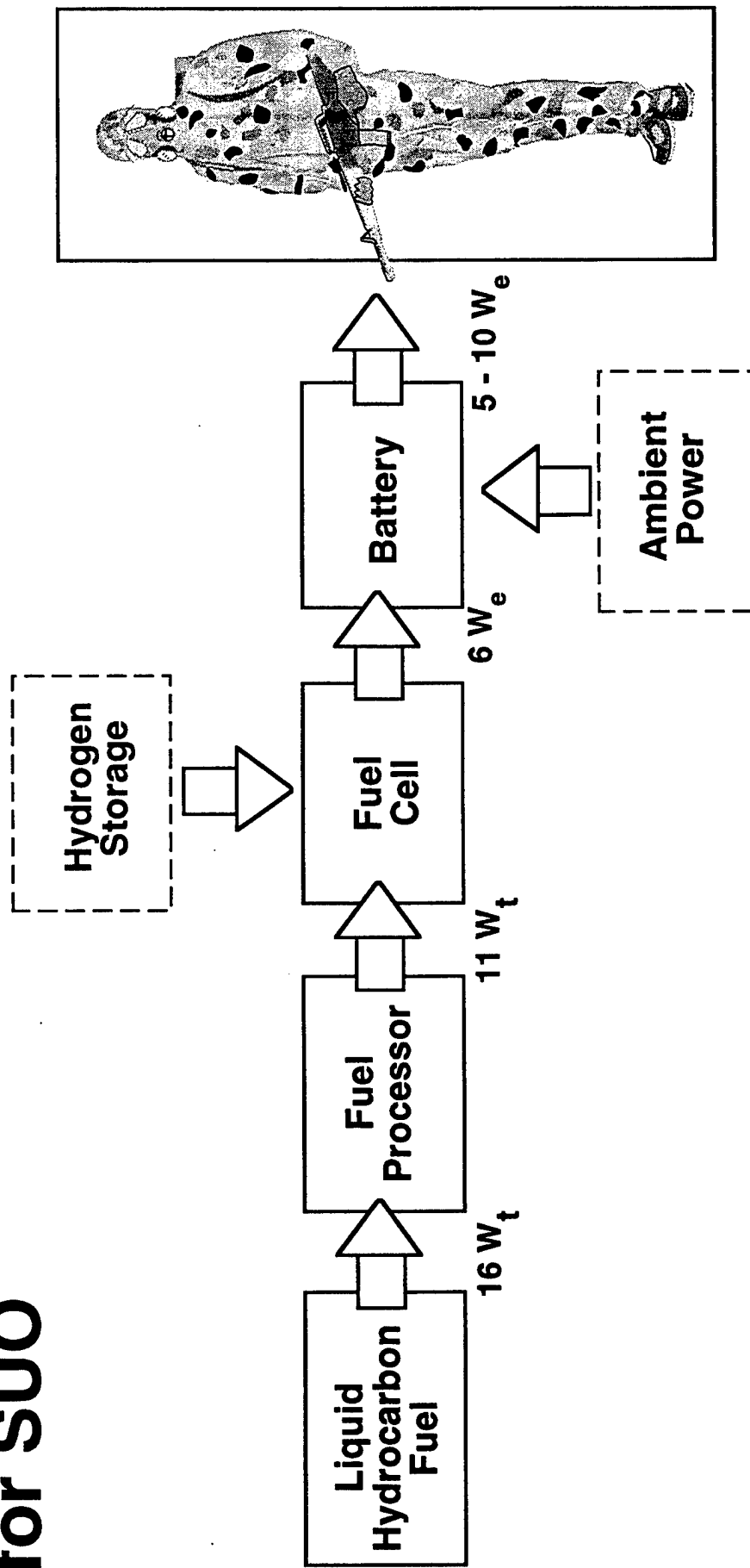- Assemble unit operations into systems

Micro Chemical Systems
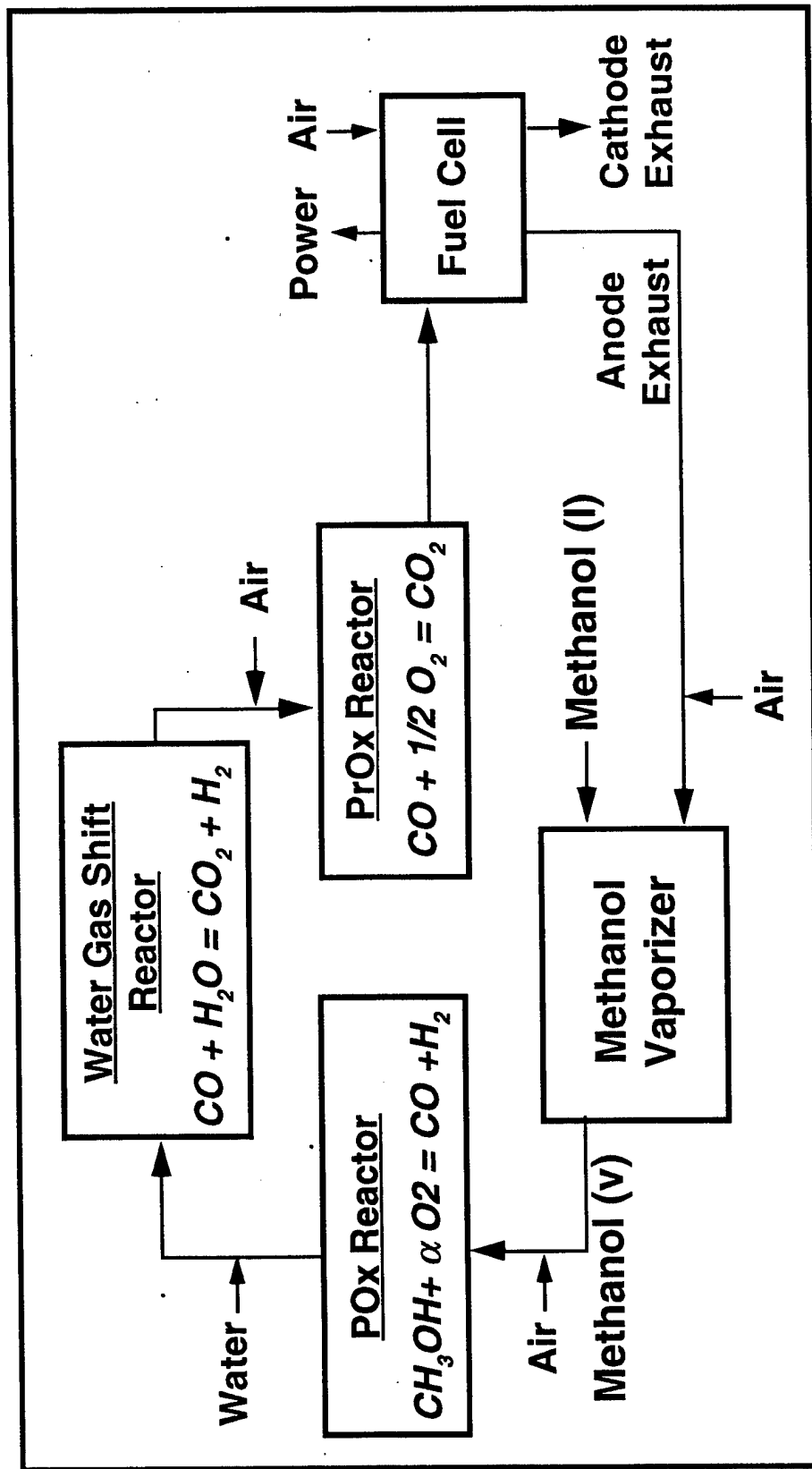
Chemical Reactor

Chemical Separator

Micro Thermal Systems

Heat Engine

Heat Pump
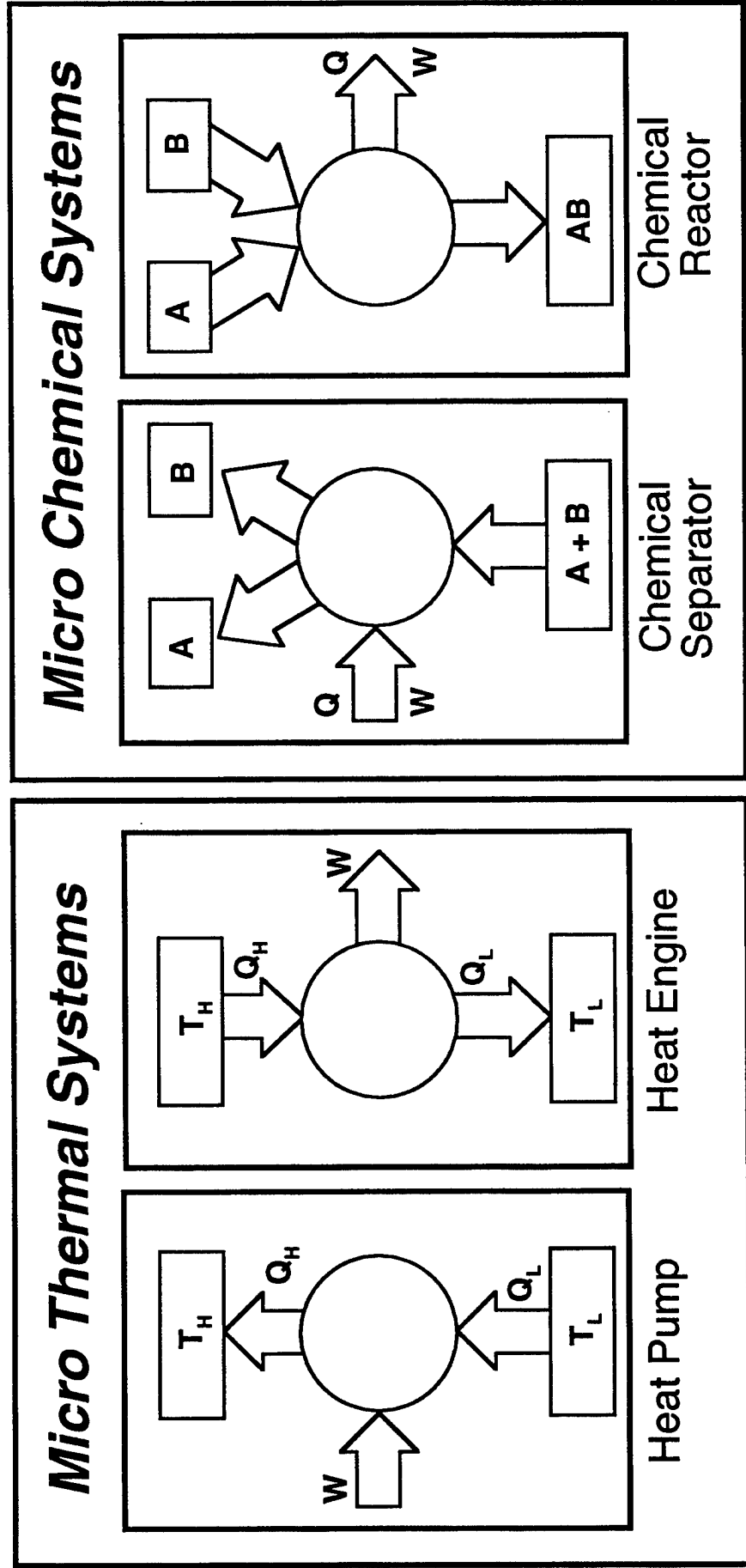
RG97040024. 21

Battelle Sheet Architecture

Patent No. 5,611,214

Manportable Power Generation Concept for SUO

| Liquid Hydrocarbon Fuel | → 16 W_t → | Fuel Processor | → 11 W_t → | Fuel Cell | → 6 W_e → | Battery | → 5 - 10 W_e → |

Hydrogen Storage → Fuel Cell

Ambient Power → Battery

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Fuel Processing System – –
Example Flow Sheet

Water Gas Shift Reactor
$CO + H_2O = CO_2 + H_2$

PrOx Reactor
$CO + 1/2\, O_2 = CO_2$

POx Reactor
$CH_3OH + \alpha\, O2 = CO + H_2$

Methanol Vaporizer

Fuel Cell

Air

Air

Water

Air

Methanol (v)

Methanol (l)

Power

Air

Anode Exhaust

Cathode Exhaust

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Example Mesoscopic Fuel Processor Configuration

Fuel Vaporizer Sheet — Fuel from Tank

POX Reactor Sheet — Air from Compressor

Air Preheat HX Sheet

Water Gas Shift Reactor Sheet — Water

Steam Superheat Sheet

PROX Reactor Sheet — Water

Steam Generator HX Sheet — Clean, Cool Fuel Gas

Fuel Gas Cooler HX Sheet

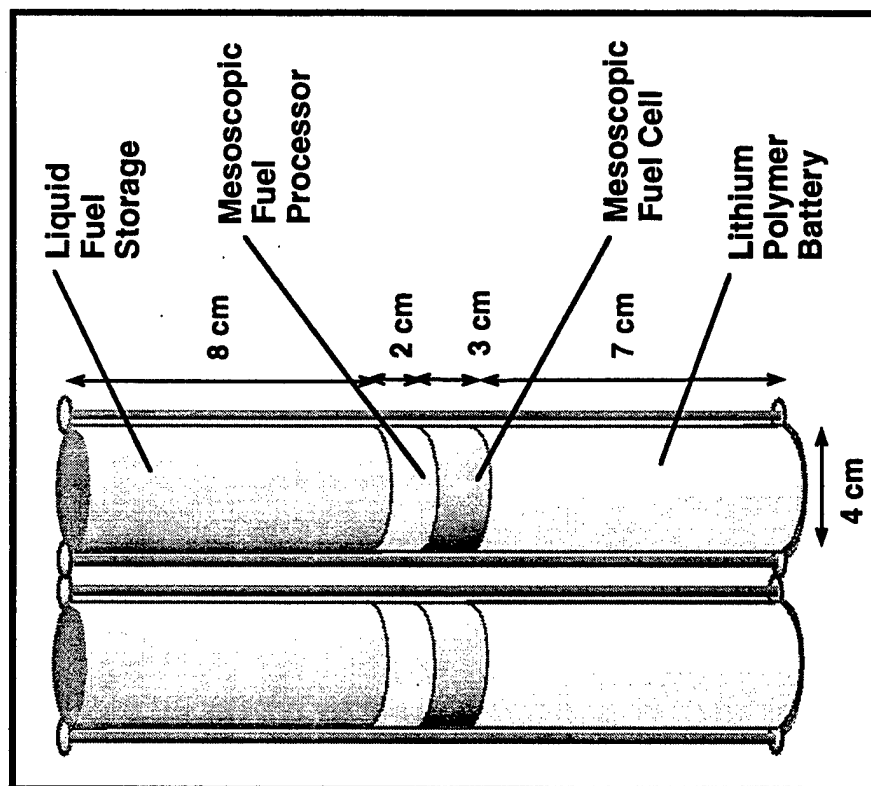☐ Microchannel Reactors Not Yet Demonstrated

244
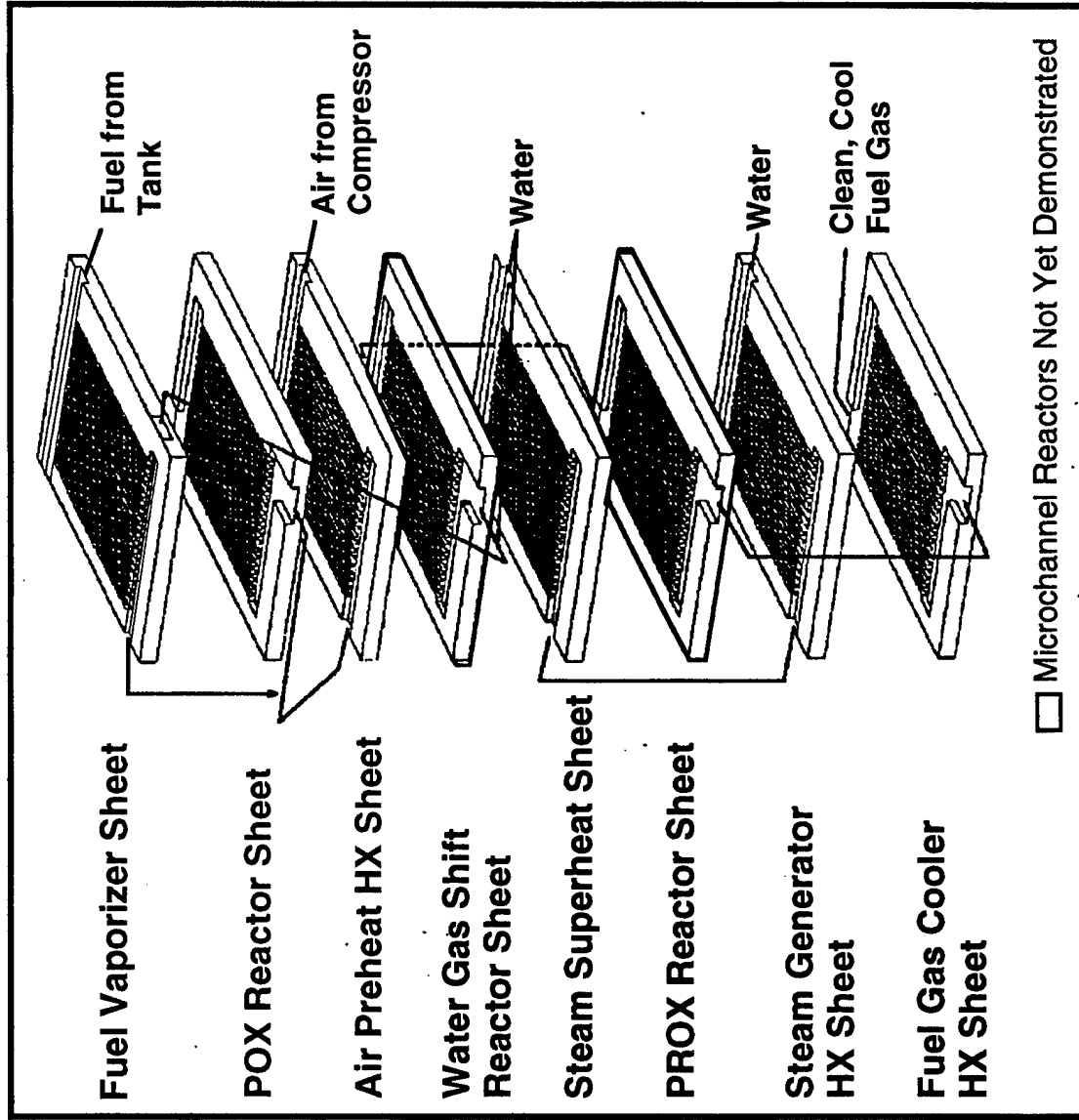
POx Test Assembly
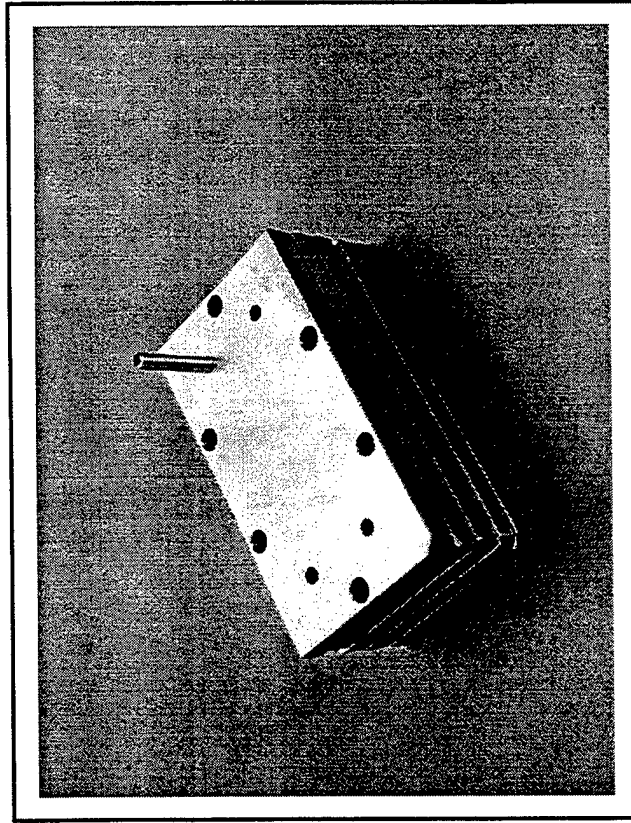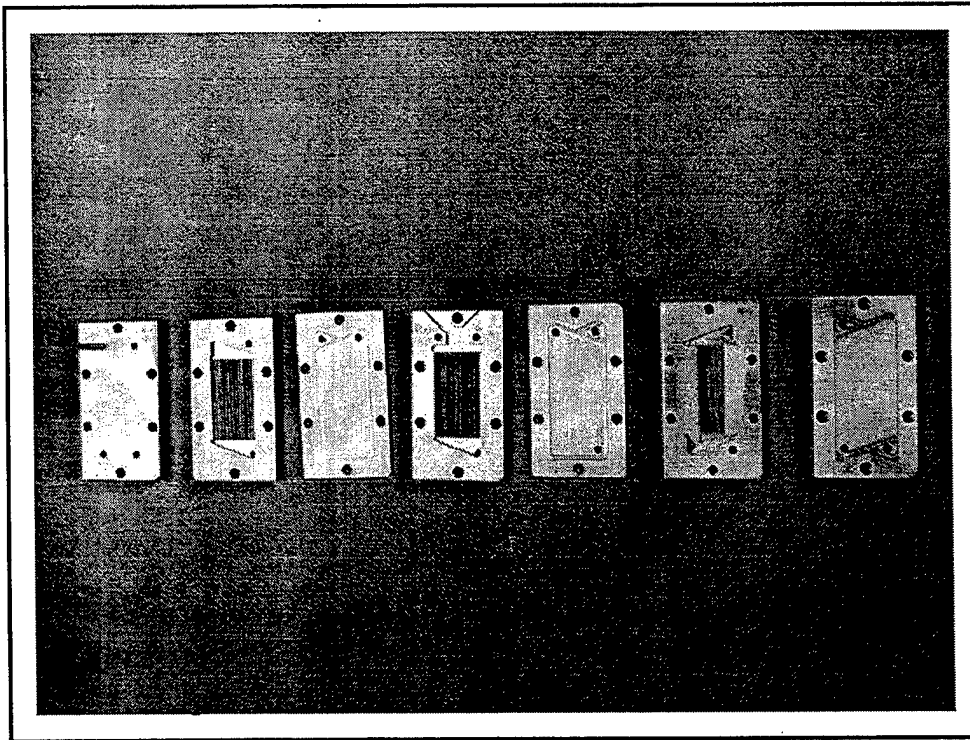
POx Test Run
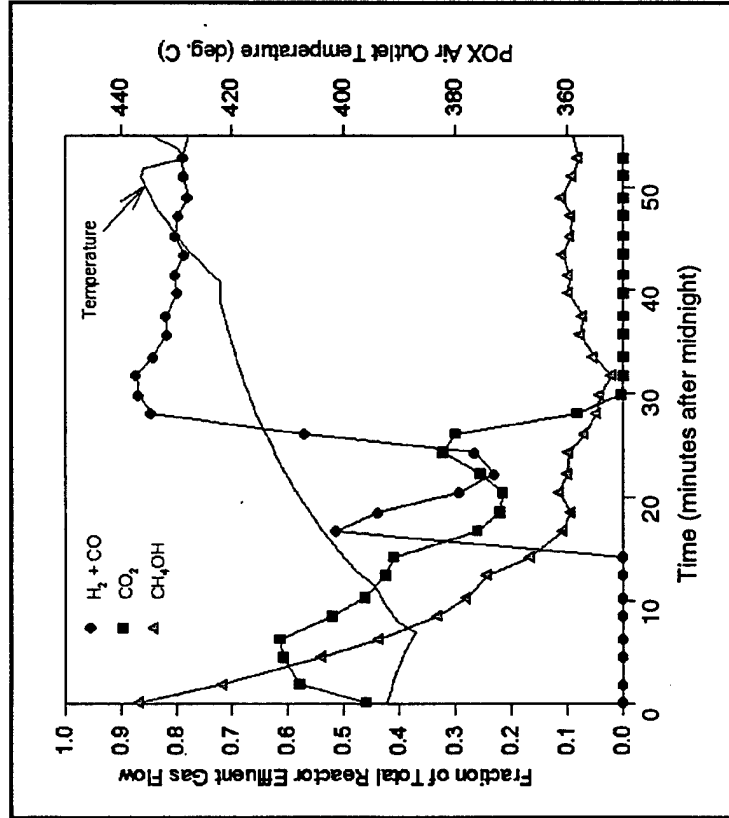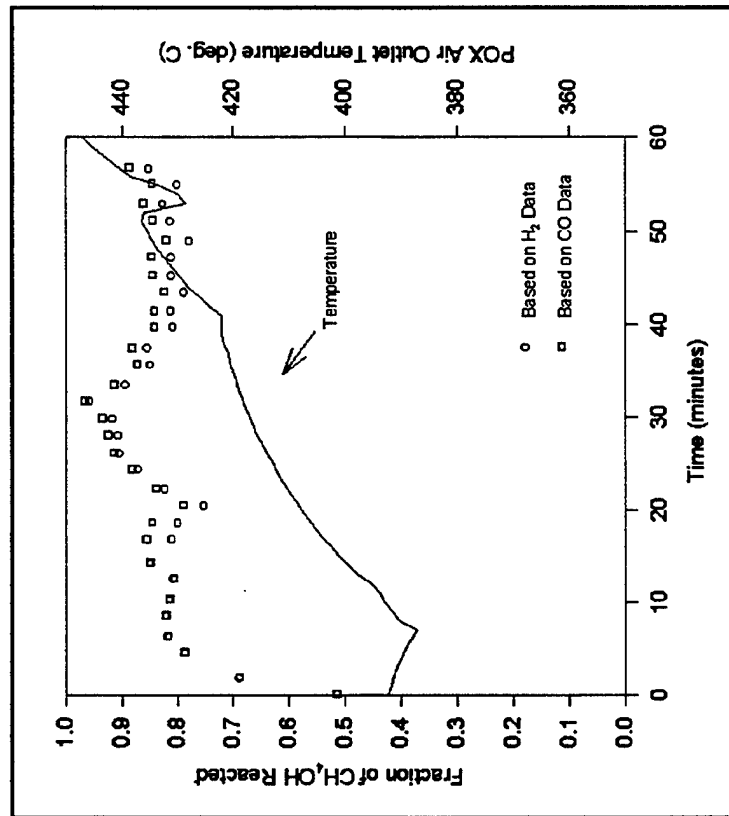
Vaporizer Status

- Demonstrated for automotive application at 1/8th of full scale

- Thermal efficiency ~75%

- Higher efficiency possible

- Full-scale version: 1" x 4" x 6"
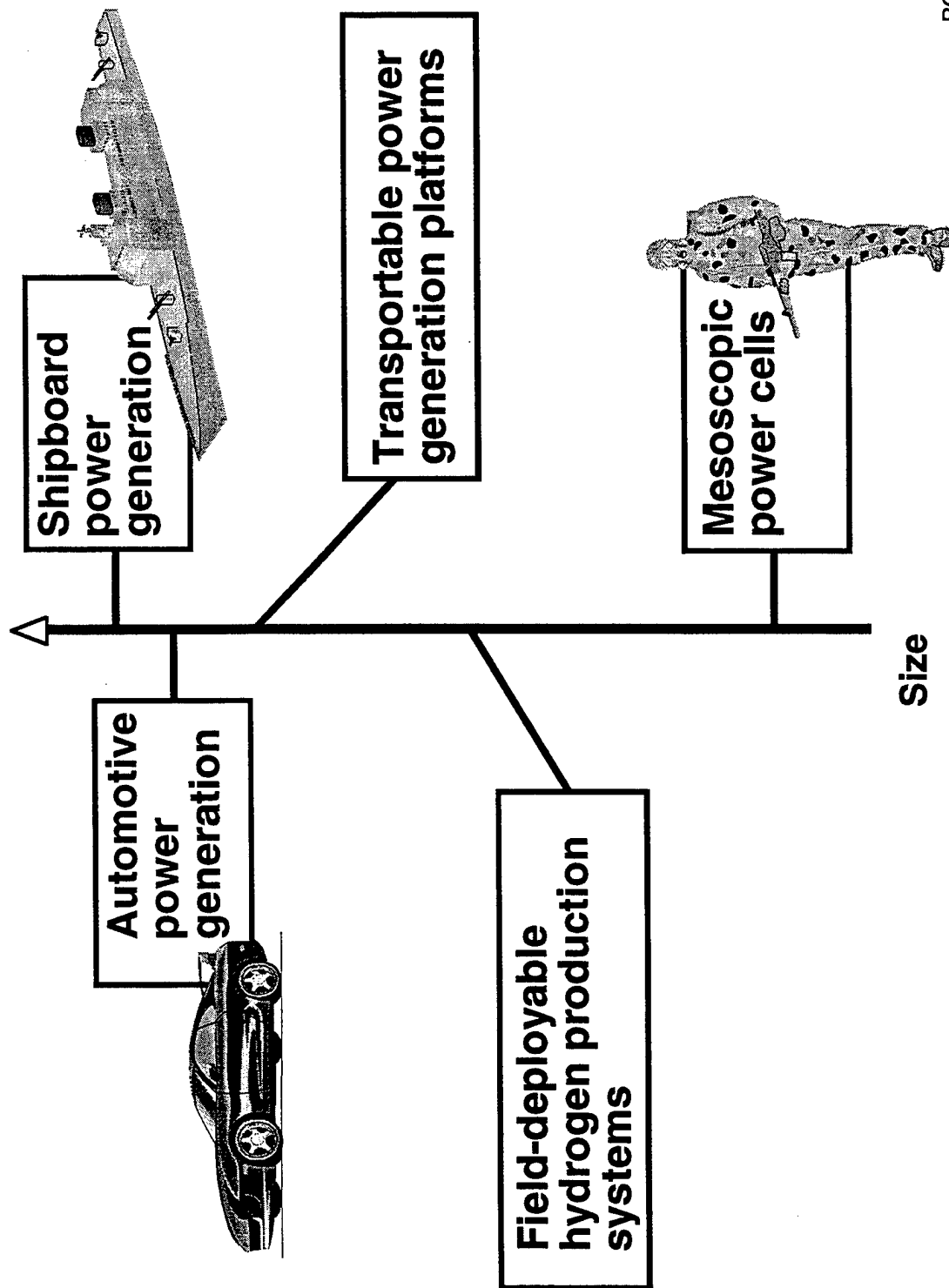
Manportable Power Generation Concept for SUO

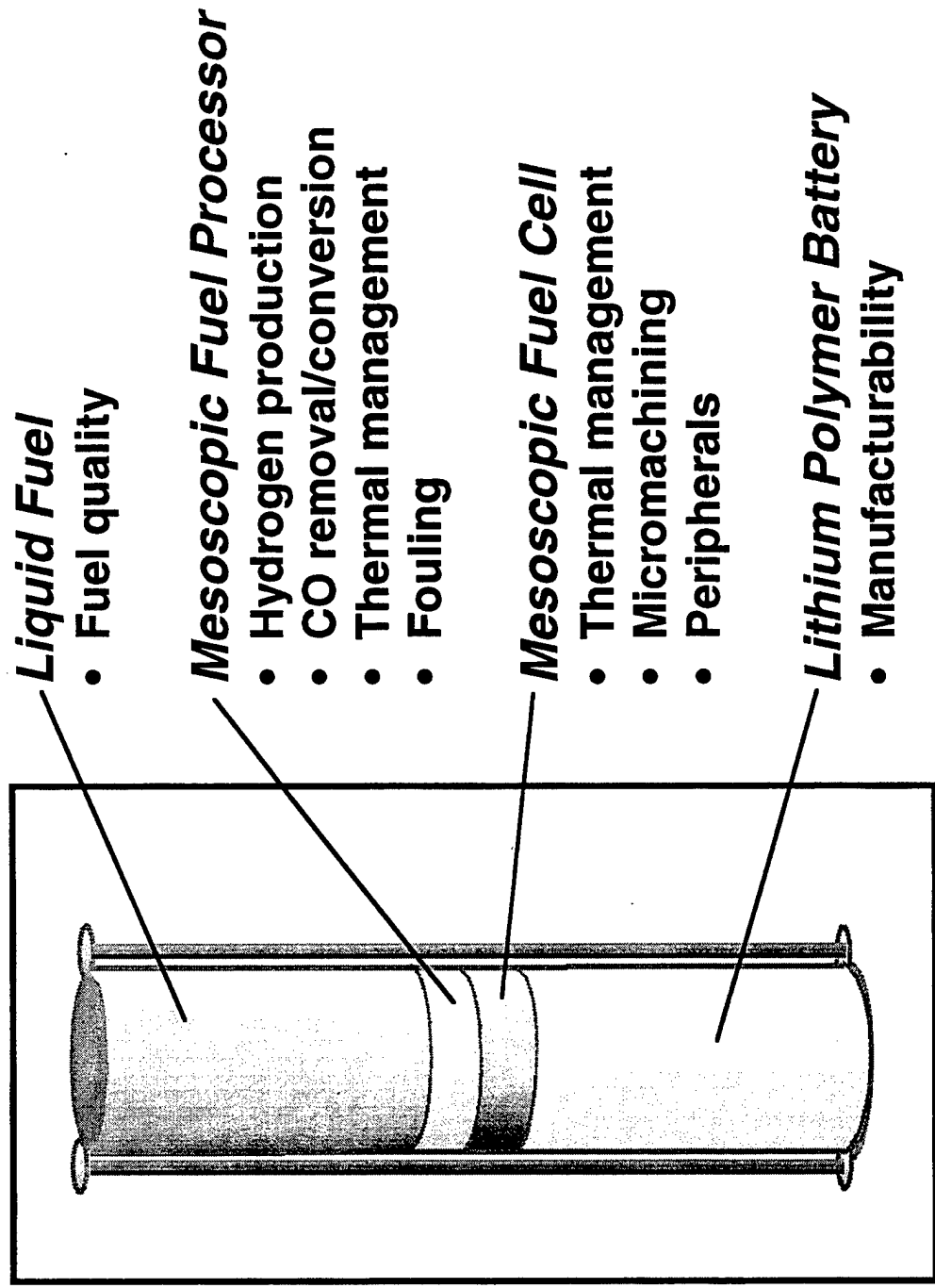| Mesoscopic Power Cell - Weight*	
Component	Weight (grams)
Fuel Cell	150
Fuel Processor	160
Fuel	200
Controls/Electronics	70
Structural	240
Battery	180
Total	1000

*A comparable battery system would weigh about 10 kg

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Multiple Deployment Scales

Shipboard power generation

Transportable power generation platforms

Mesoscopic power cells

Automotive power generation

Field-deployable hydrogen production systems

Size

Mesoscopic Power Cell -
Technical Challenges

Liquid Fuel
- Fuel quality

Mesoscopic Fuel Processor
- Hydrogen production
- CO removal/conversion
- Thermal management
- Fouling

Mesoscopic Fuel Cell
- Thermal management
- Micromachining
- Peripherals

Lithium Polymer Battery
- Manufacturability

Future Plans

- **Continue to investigate utilization of high-energy density liquid hydrocarbons (e.g., JP-8, diesel fuel)**

- **Continue to investigate operational characteristics and system dynamics for POx-based system platform**

- **Investigate alternative system flowsheets and components, including steam reforming and membrane separations**

Summary

- **Mesoscopic fuel processing systems may be small in comparison to the energy storage medium (liquid hydrocarbons or hydrogen)**

- **System weight can be further reduced by including a battery to meet peak power requirements**

- **Deployment modes for manportable power generation include:**
  - **Integrated fuel processors/fuel cells (mesoscopic power cells)**
  - **Field-deployable fuel processing to support hydrogen-based units**

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Partial Oxidation of Hydrocarbons

Jack Frost

Workshop on Hydrogen Storage and Generation
Orlando, Florida April 1997

Hydrocarbon Reforming

Methods

- Hydrogen from hydrocarbons

- Thermal
- Steam reforming
- Non catalytic partial oxidation
- Catalytic partial oxidation
- Autothermal reforming

- Fuel selection

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Partial Oxidation

Catalytic partial oxidation of methanol

- Partial oxidation
- $CH_3OH(l) + 1/2O_2 \rightarrow CO_2 + 3H_2$ $-160kJ/mol$

- Steam reforming
- $CH_3OH(l) + H_2O(l) \rightarrow CO_2 + 3H_2$ $+133kJ/mol$

- Rapid start up
- Compact and flexible
- Heat integration
- CO formation

JM Catalyst Technology

Examples of current and past activity

- Sud-Chemie / VW
- Rolls Royce
- British Gas
- CJB
- Haldor Topsoe

- AD Little
- Argonne National labs
- JPL

- Johnson Matthey

Catalyst Technology
JM

Original Design: Performance Characteristics

Reaction Stoichiometry

$$CH_3OH + 1/2\ O_2 \rightarrow 2H_2 + CO_2$$

Reformate composition

40% H_2, 18% CO_2, 2% CO, 40% N_2

Start-up time

15-30 minutes

Steady state output

10-20 l.h^{-1} of hydrogen from 1 l reactor

Other fuels sucessfully reformed:

natural gas (methane)
propane (LPG)
n-hexane
petroleum ether
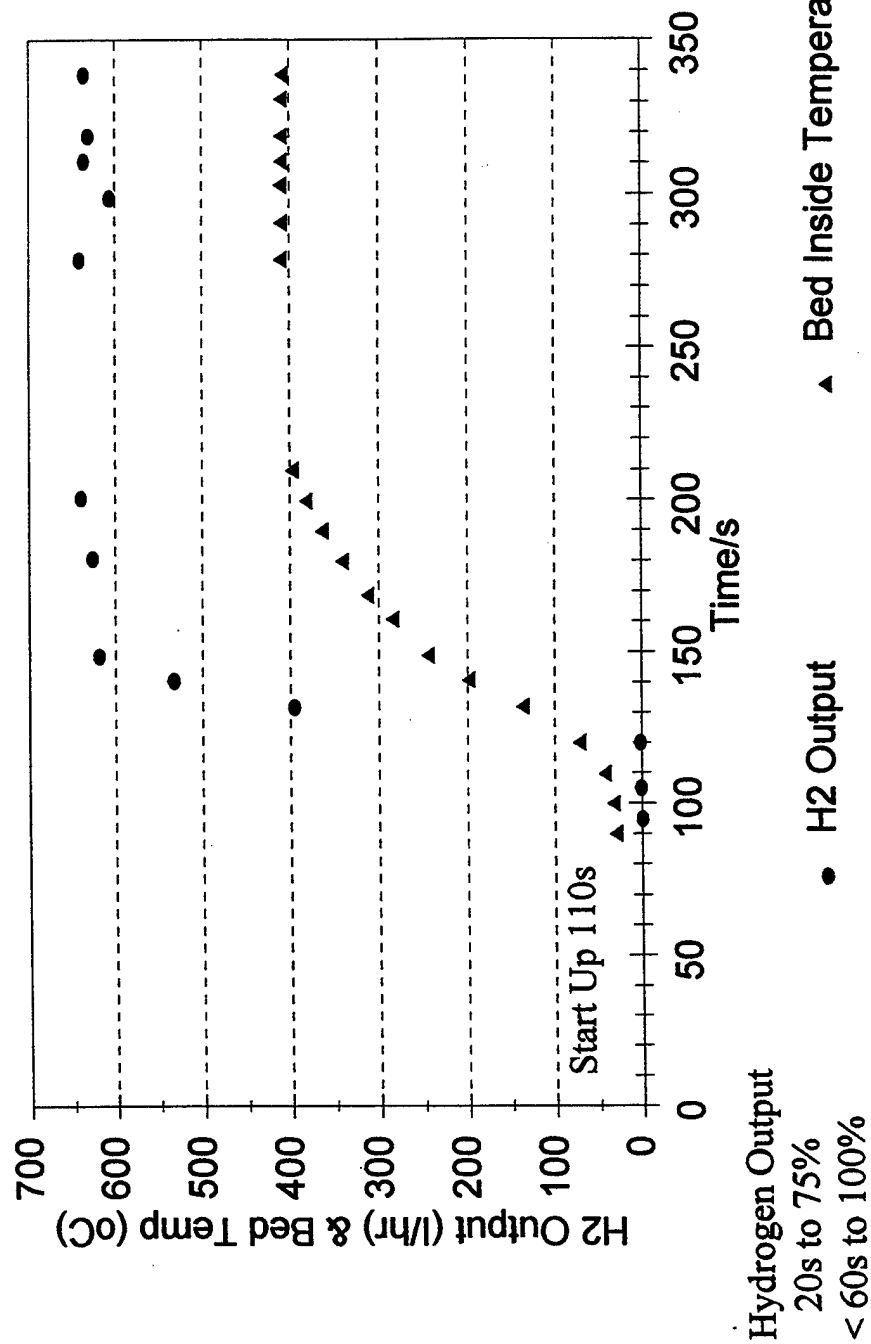lead-free gasoline

UM **Catalyst** Technology

257
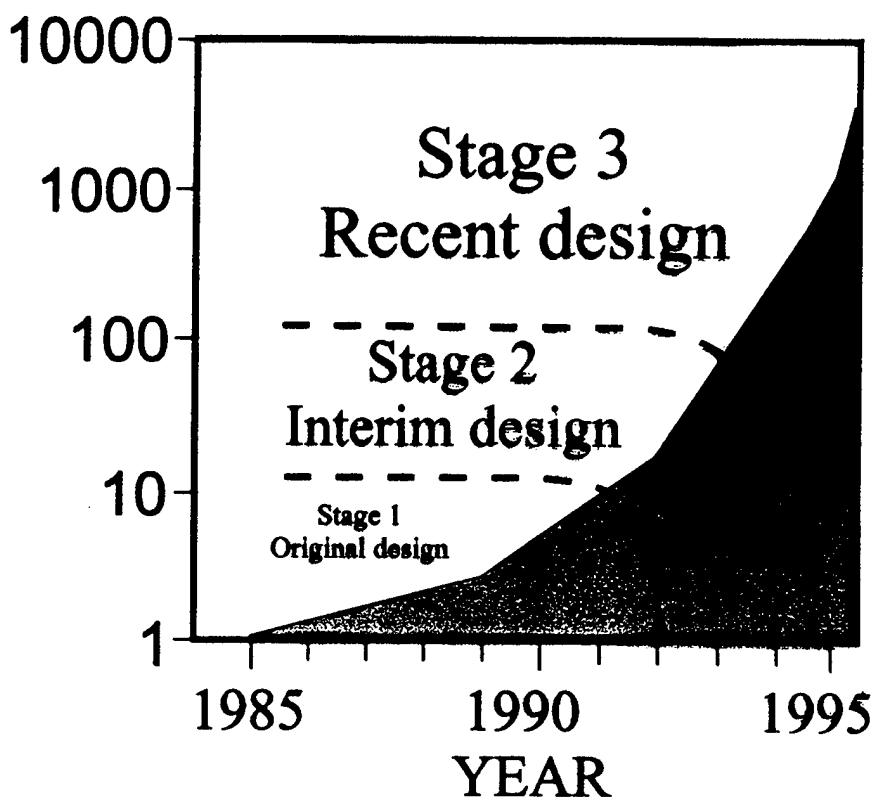
PMR Start Up

T < 400C MeOH:O2 ratio = 3.7
T > 400C MeOH:O2 ratio = 4.4

Hydrogen Output
20s to 75%
< 60s to 100%

● H2 Output   ▲ Bed Inside Temperature

Commercial in Confidence

259

Steady State Performance of Single Unit

100% Conversion

260
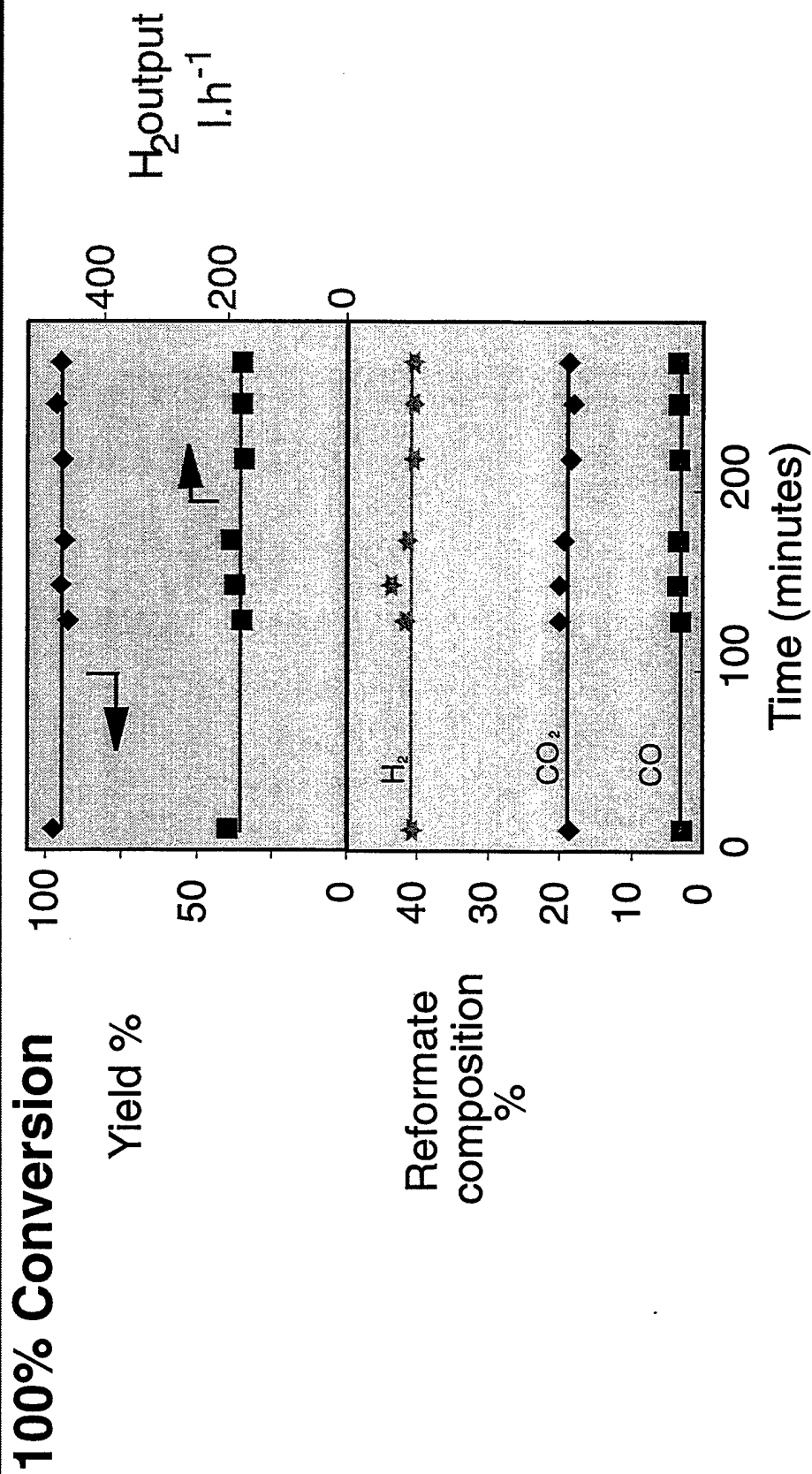
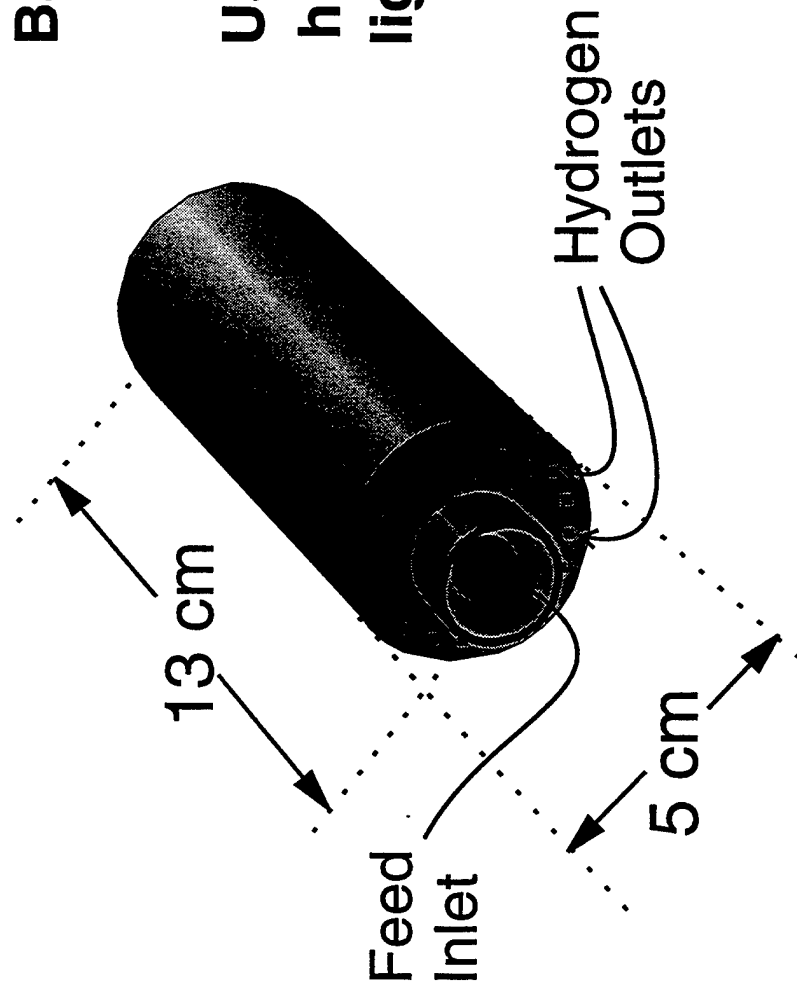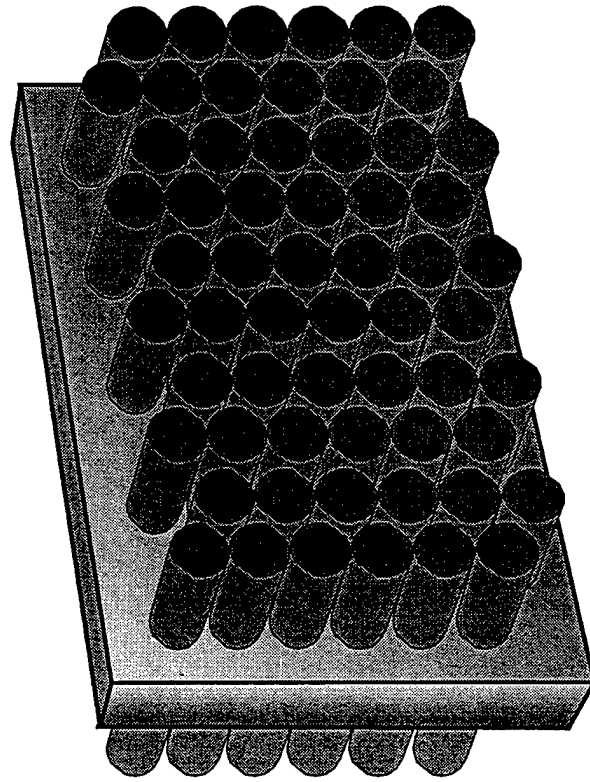# Steady State Performance of Single Unit

Fuel-rich conditions
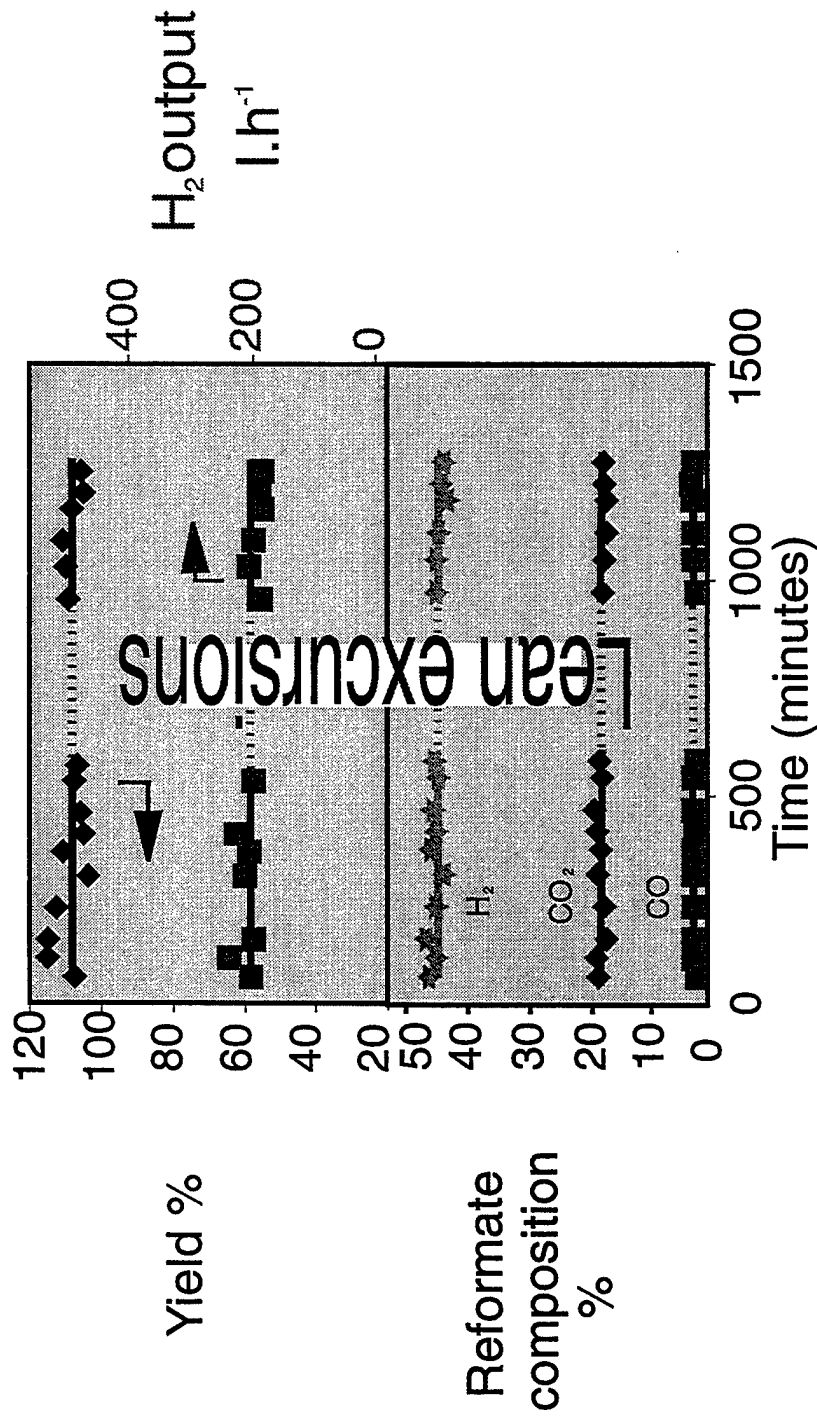
JM Preferred Design

Based on proven technology

Uses an array of compact, highly productive, fast light-off, hot-spot, reactors

13 cm
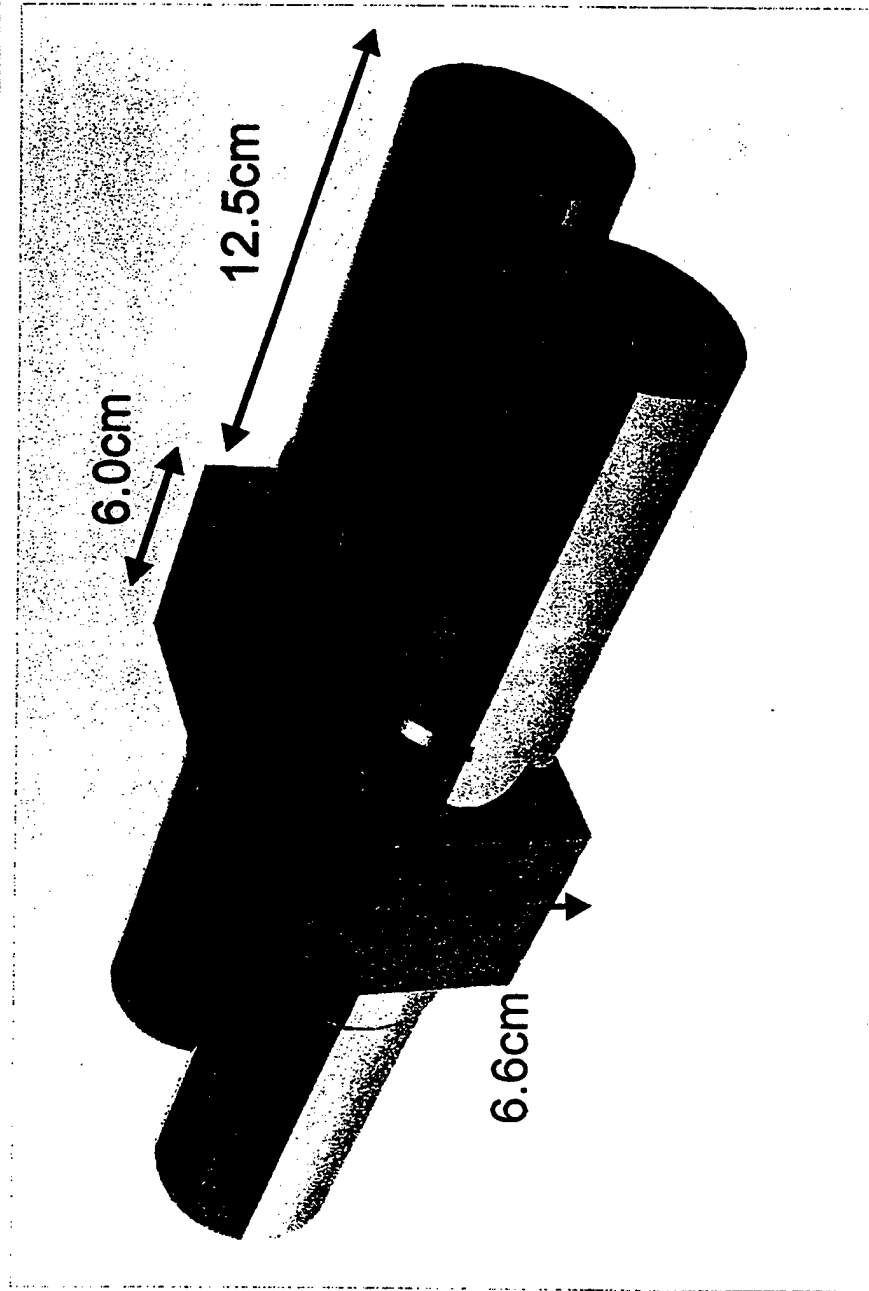
5 cm

Feed Inlet

Hydrogen Outlets

Features

- proven reactor technology;
- modular design;
- rapid heat loss from reactor;
- incoming feed heated by outgoing gases;
- simple servicing and module replacement.

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4 KMR Unit Reformer

12.5cm

6.0cm

6.6cm

JM Catalyst Technology

Current Hot-Spot Unit

Volume	$245 cm^3$
Total internal mass	250g
Catalyst mass	30g
Start-up time	20s to 75% output
	>60s to 100% output
Reaction mechanism	partial oxidation and steam reforming
Reaction stoichiometry	$2.3 mol\ H_2 / mol\ CH_3\ OH$
H_2 concentration	55%
H_2 output	$625\ l.h^{-1}$
Catalyst specific H_2 output	$11,000\ l.h^{-1}\ l^{-1}$
Reactor-specific H_2 output	$2,550\ l.h^{-1}\ l^{-1}$

Fuel Cell Reformate System

266
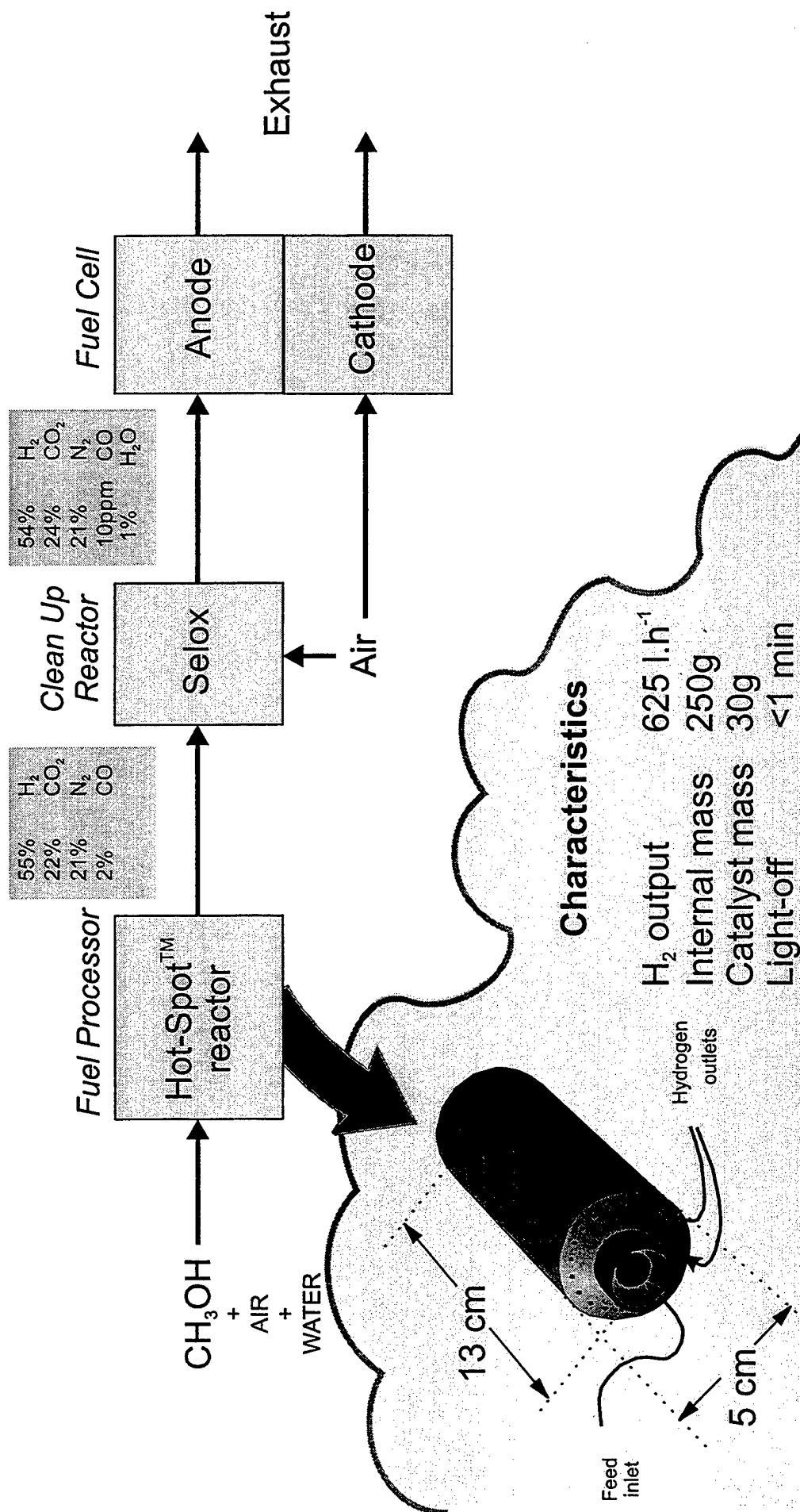
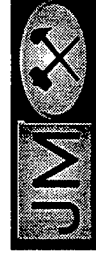# Hot Spot Reformer: Gas Clean-Up

JM proprietary SELOX reactor

In tests using wet synthetic reformate
(5% CO, 15% CO_2, 40% H_2, 40% N_2)

- CO attenuated to < 5ppm
- reformate space velocity:14000 h^{-1}
- operating temperature: 220°C
- only 2.5% of total available H_2 consumed

Scale-up prediction:

25l (30kW) Hot Spot reformer requires 5l SELOX reactor

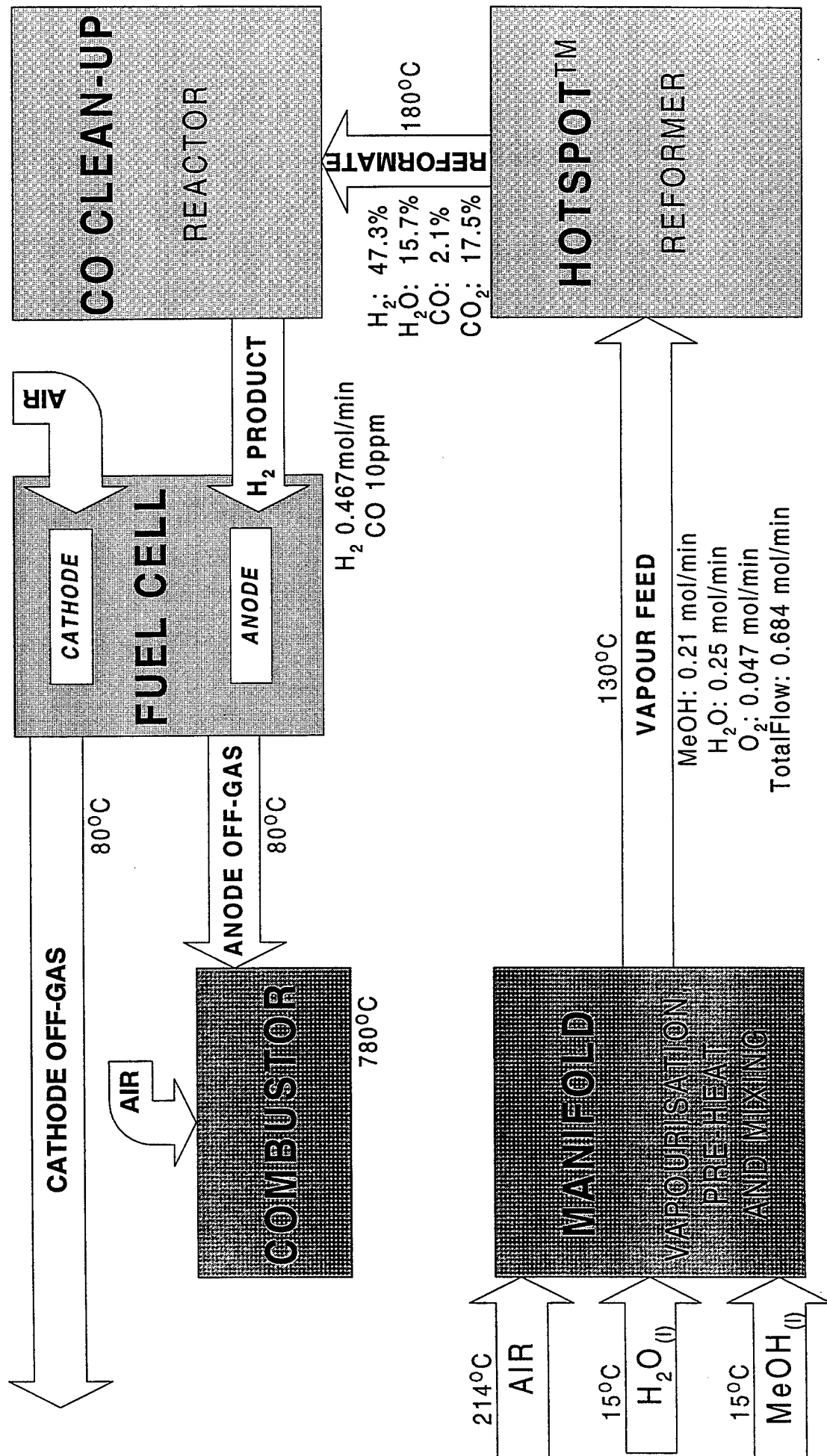# Conclusions: Current Hot-Spot Reactor

- compact
- partial oxidation + steam reforming
  = high output

- low thermal mass = rapid start-up
- excess energy available
  for extra steam reforming
- radical modular reformer design

Future directions:

reforming of alternative fuels
tailoring to specific applications

BASE CASE

CO CLEAN-UP REACTOR

FUEL CELL
CATHODE | ANODE

H_2 PRODUCT

H_2 0.467mol/min
CO 10ppm

AIR

CATHODE OFF-GAS

80°C

80°C

ANODE OFF-GAS

COMBUSTOR

AIR

780°C

REFORMATE

180°C

H_2: 47.3%
H_2O: 15.7%
CO: 2.1%
CO_2: 17.5%

HOTSPOT™ REFORMER

130°C

VAPOUR FEED

MeOH: 0.21 mol/min
H_2O: 0.25 mol/min
O_2: 0.047 mol/min
TotalFlow: 0.684 mol/min

MANIFOLD
VAPOURISATION,
PRE-HEAT
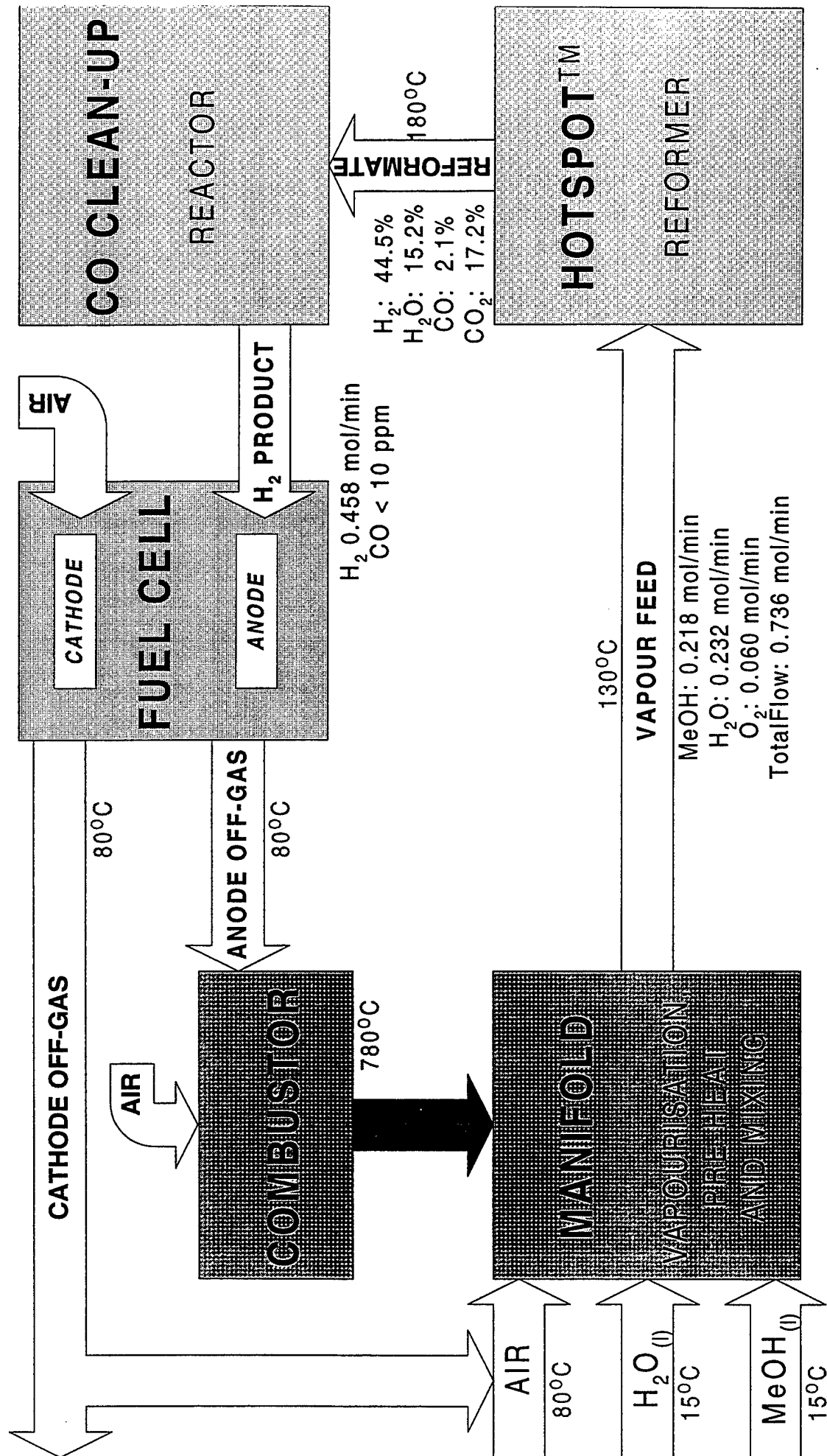AND MIXING

214°C
AIR

15°C
$H_2O_{(l)}$

15°C
$MeOH_{(l)}$

Catalyst Technology

UM

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THERMALLY NEUTRAL CASE

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Person portable power

- Current HotSpot +CO clean up
  - Hydrogen yield @1kW, 1.13kg, 0.85 litre
  - Allowing for H_2 utilisation and parasitic power
  - Hydrogen yield @0.5kW
  - Scale to 300W usable power
  - 0.77kg and 0.51 litre

- Design improvements due soon
  - 0.53kg and 0.51 litre

Person portable power

- Ancillary items
- Fuel tank methanol + water
  - 1kWh - 1.53l ;   10kWh 15.3l;   90kWh 137.7l
- Air blower
- Pumps
- Cooler before fuel cell
- Exhaust treatment

Partial Oxidation

Summary

- System weight and volume determined by the fuel tank

- 300 W 10kWh system
  - Approx 15 kg and 16 litre including fuel and water
- 100W 1 kWh system
  - Approx 2 kg and 2 litre including fuel and water
- 10W 90kWh system
  - Approx 130 kg and 130 litre

- Water recirculation could half the wt and volume

UMIX

Catalyst
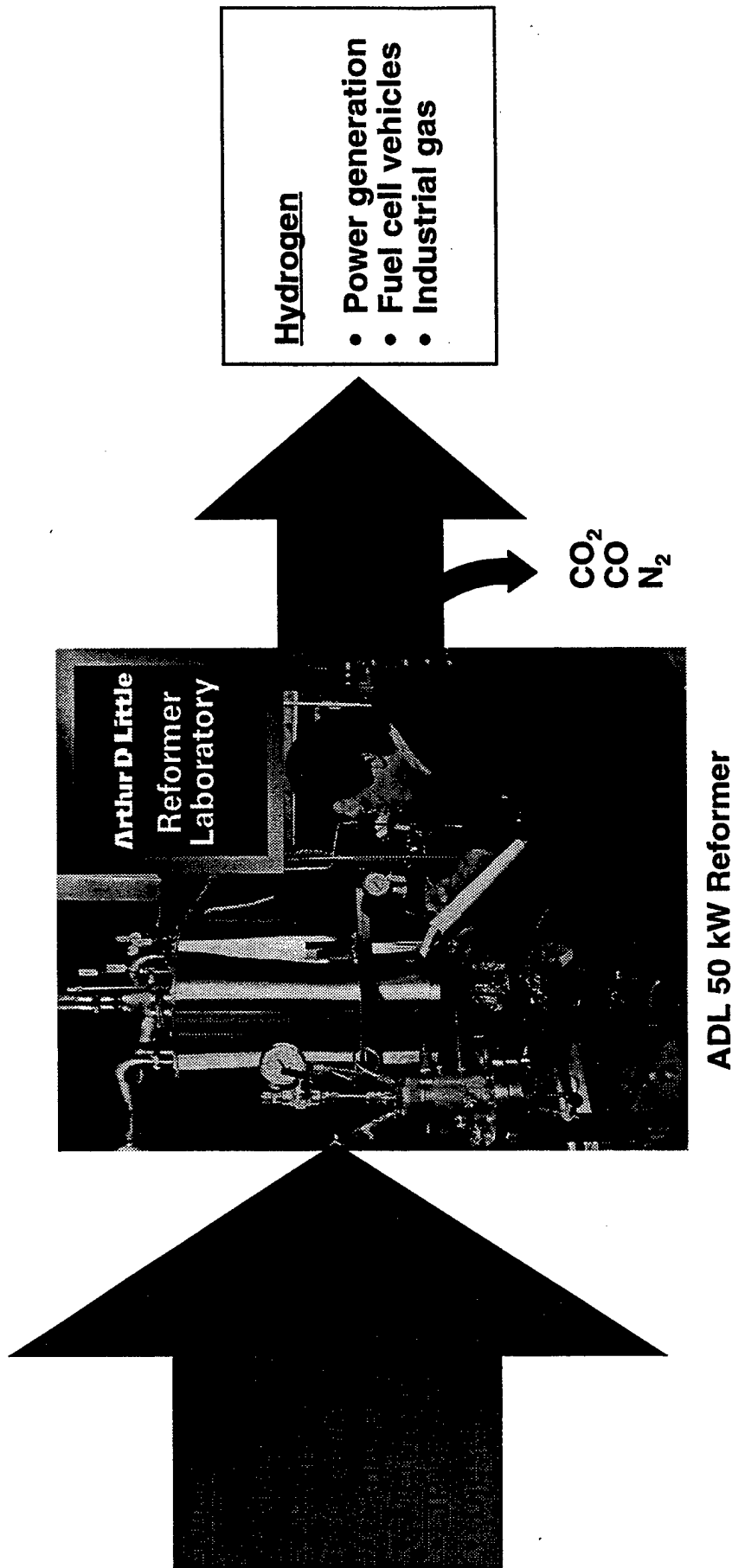Technology

273

Small-Scale Fuel Flexible Fuel Processors

**Presentation to
Workshop on Storage and
Generation of Hydrogen**

April 8, 1997

Arthur D. Little, Inc.
Acorn Park
Cambridge, Massachusetts
02140–2390
(617) 498–5000

Reference 93275

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The Arthur D. Little Fuel Processor converts common fuels to hydrogen for a variety of applications.

Arthur D Little
Reformer Laboratory

ADL 50 kW Reformer

CO_2
CO
N_2

Hydrogen
- Power generation
- Fuel cell vehicles
- Industrial gas

1

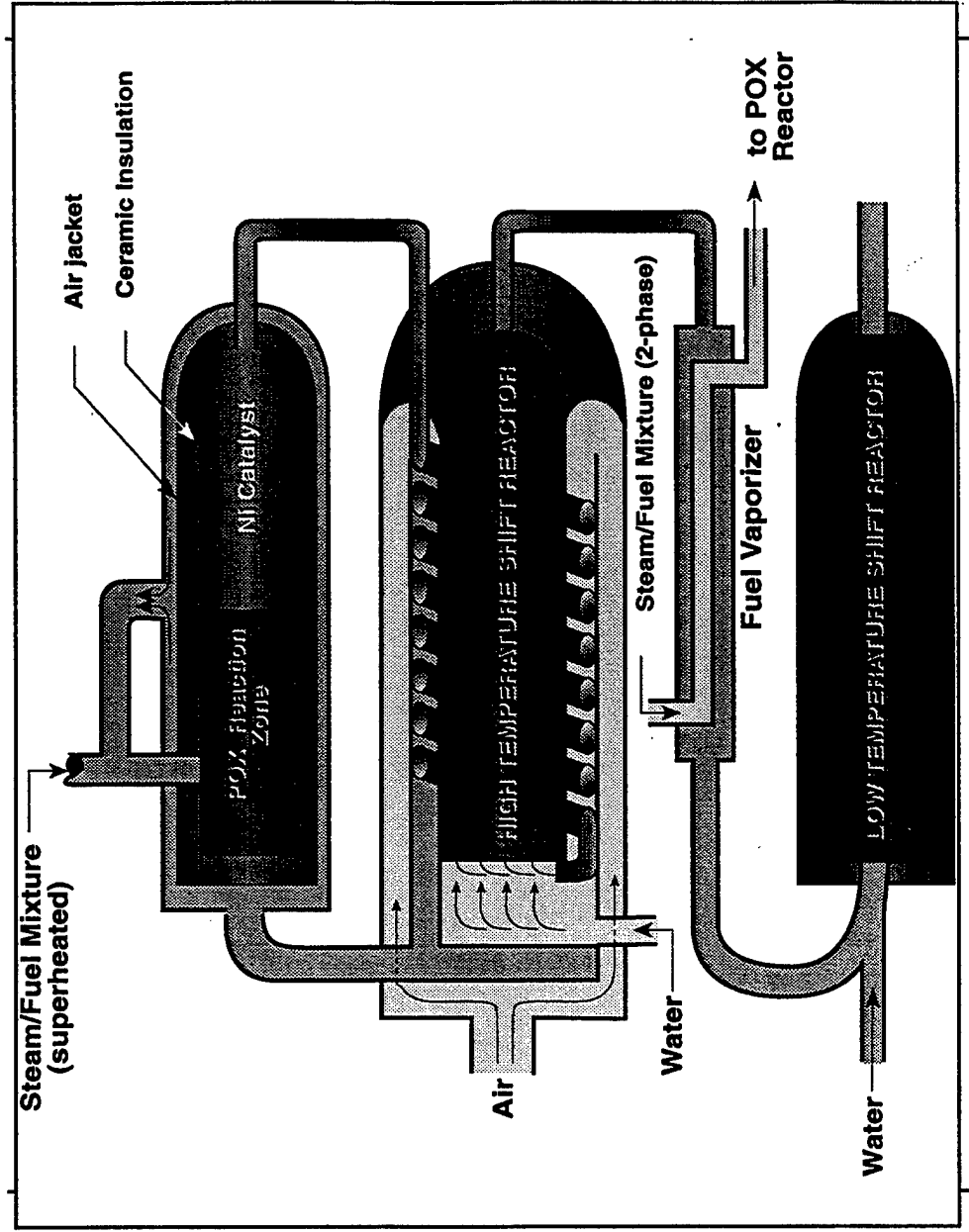Fuel Processor Technology   50 kW Fuel Processor

Integrated construction cuts cost, weight, and volume while minimizing thermal loss.

50 kW Conceptual Layout

Features:
- POX Reactor
- Ni Catalyst
- HTS Reactor
- LTS Reactor
- Air Preheater
- Steam Generator

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The Arthur D. Little Fuel Processor has demonstrated several critical performance achievements.

- Over 3,000 hours of operation at 10-50 kW$_e$

- Operation with fuels of major interest

  - Natural gas

  - Propane

  - Alcohols

  - JP-8

- On-line fuel switching with no hardware change

- Integration with PROX to achieve 50 ppm CO on gasoline

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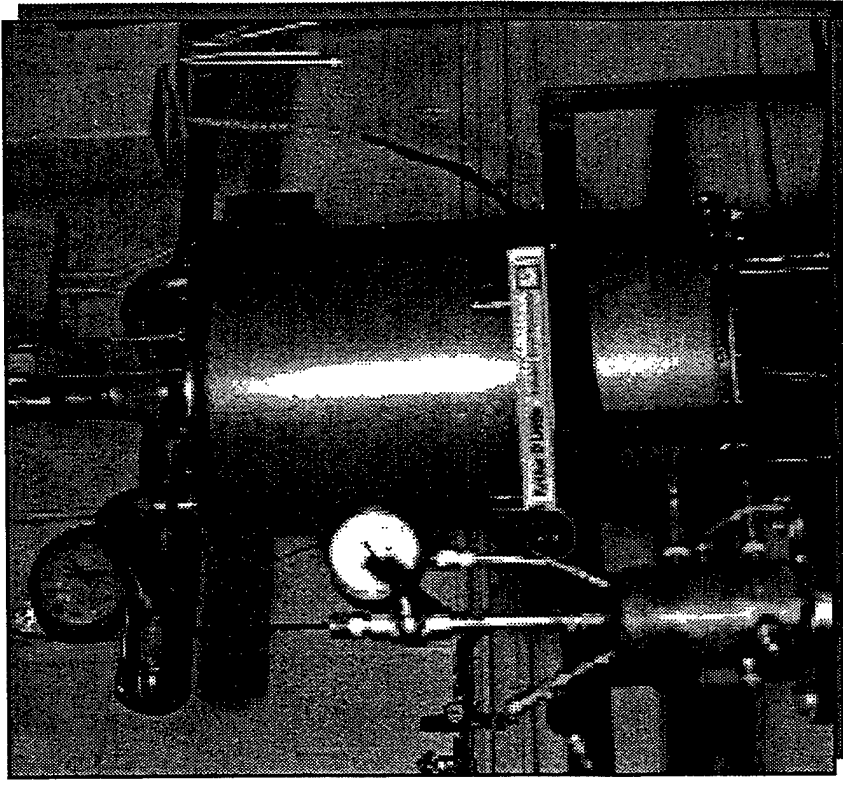
The petroleum fuel processor program has been successfully completed, leading to heightened Automotive Industry interest in this DOE funded work.

- All key design objectives met:
  - Low-cost steam generator
  - Redesigned air preheater
  - Integral sulfur removal bed
- Baseline testing has been successfully completed
  - 1-3 atm, 50 kW$_e$ max, 7:1 turndown
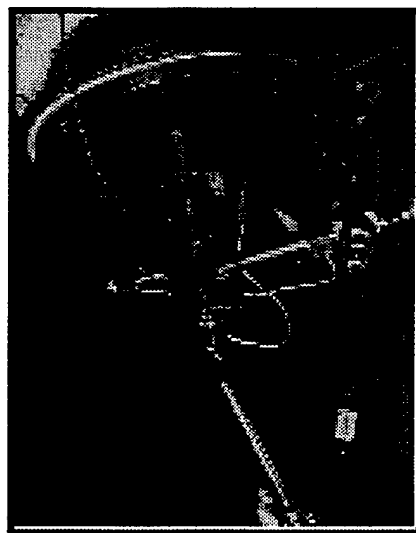- Integration and testing with PROX has been successfully demonstrated
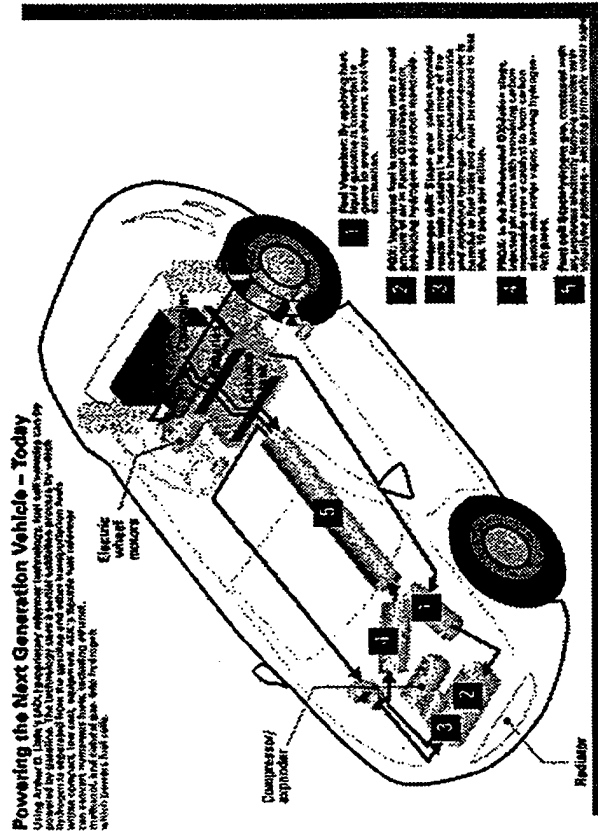
The feasibility of operation on multiple fuels such as renewable ethanol and normal reformulated gasoline has been demonstrated in this program.

Powering the Next Generation Vehicle – Today

The fuel processing modules incorporate new design features to performance in the range of 50-300 watts

- Basic physical phenomena are same as in well-demonstrated larger-scale equipment

- High surface/volume characteristics allow highly favorable design strategies not practical in larger capacities

- Reactant flow paths modified to reduce thermal losses and pressure drops (often issue with very small-scale systems) to negligible levels

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A family of low-cost, small-scale hybrid POX fuel processors have been developed for atmospheric operation on multiple fuels.

Reformate Outlet

Air Inlet

300 W$_e$ Hybrid POX Fuel Processor

Fuel

8.6"

6.0"

1 kW$_e$ POX Reformer

Reformate Outlet

Air Inlet

50 W$_e$ Hybrid POX Fuel Processor

Fuel

5.2"

4.25"
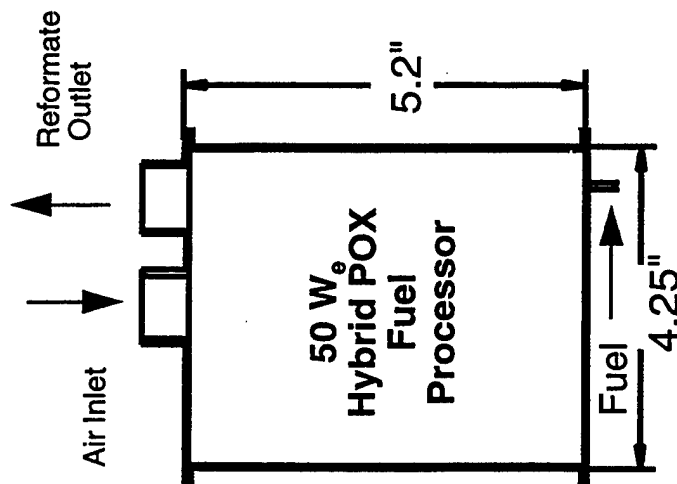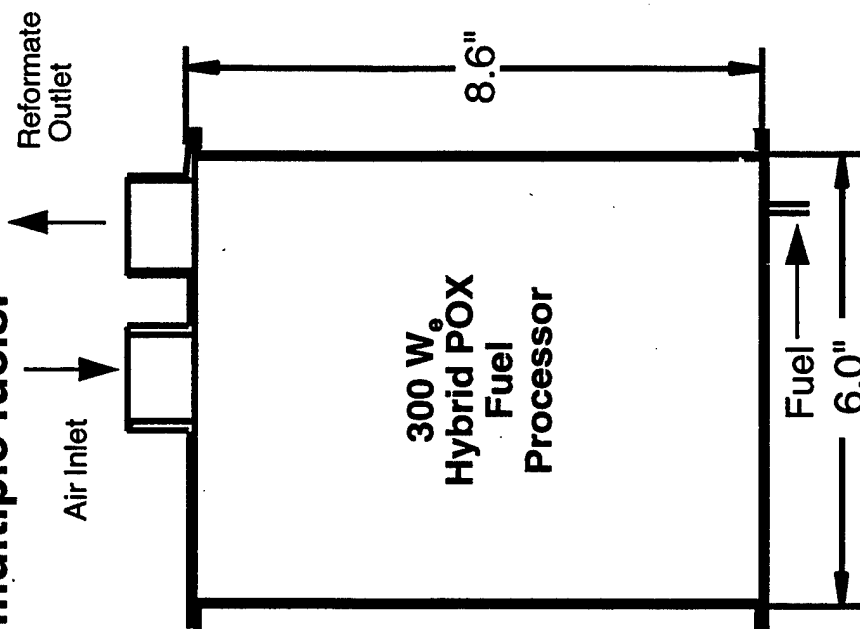
Modules drawn include hybrid POX reformer, shift reactors, PROX, and associated hardware.

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Promising PROX catalyst testing is being conducted on a micro-reactor at Arthur D. Little.

Catalyst characteristics:
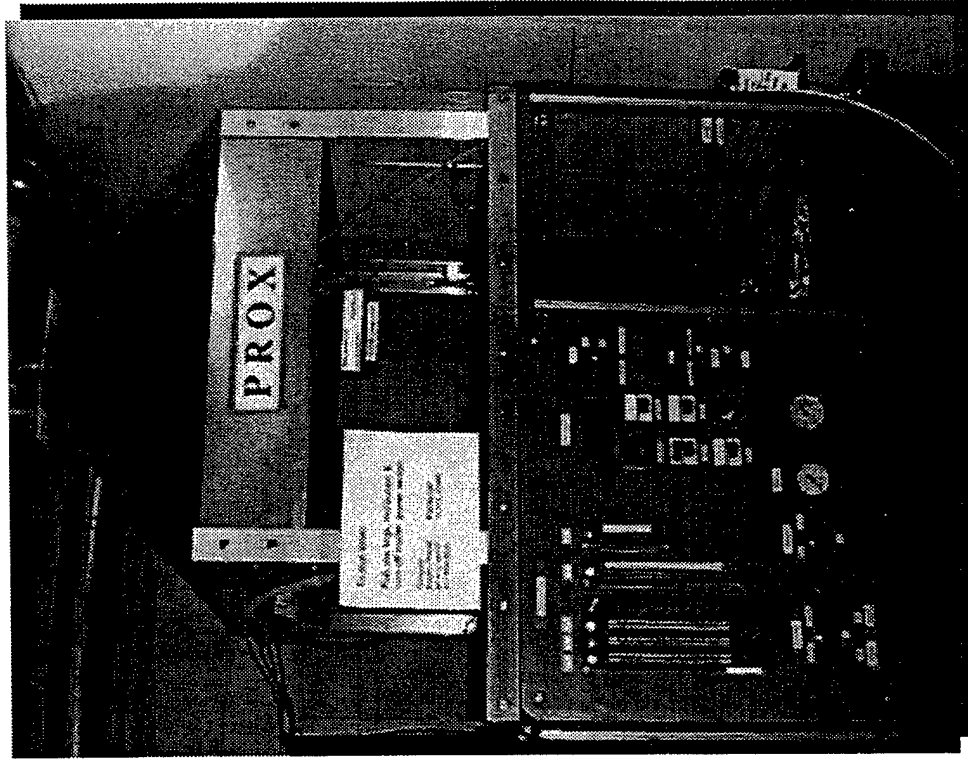
High catalyst activity at 120° C $\left(2\frac{\text{mmol CO}}{\text{sec g}_{\text{catalyst}}}\right)$

Low hydrogen consumption (< 1 %)

Activation energy (8 kcal/mol)

At least 20 times more active and more selective than conventional catalysts based on Pt

The technology is in the process of being fabricated/tested at scale appropriate for 50-300 watt fuel processing systems.

8

ADL is giving particular attention to the "auxiliaries" required for practical operation in meso-scale units (below 100 watts)

- "Auxiliaries" are those components needed to supply

  – Partial oxidation air

  – Fuel pumps and valves

  – Controls

- Very low flow rates require technology strategies quite different from those used in larger capacities

- ADL considering multiple technology options:

  – Meso-scale Scroll pumps and blowers

  – Piezo-Electric Whisper Fans

  – Metering pumps

Commercial, high-efficiency versions of these critical auxiliaries are, in general, not readily available at the lower end of the power range.

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Fuel Processing at ADL

Complementary technology development programs add further value to our fuel processor programs.

- Low-cost, efficient hydrogen storage technology (metal hydride/phase change material)

- Scroll compressor/expander

- Preferential oxidation of CO (novel catalyst under development)

- Low-cost control system based on automotive components

- Cost and performance models for fuel processing systems and their interface with fuel cell stacks

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ABSTRACT

METAL HYDRIDES AS HYDROGEN STORAGE MEDIA

J. J. Reilly
Department of Applied Science
Brookhaven National Laboratory
Upton NY, 11973
USA

Presented at the Workshop For Hydrogen Storage and Generation
Technologies for Medium Power and Energy Applications
April 8-10, 1997

Hydrogen is a potentially cheap and non-polluting fuel which
can be used in many different types of energy converters,
including fuel cells. However, a major problem, which must be
solved before it can be widely and commonly used in this context,
is the difficulty involved in storage and portability of
hydrogen. Currently hydrogen is stored as a compressed gas or as
a cryogenic liquid; while the latter may he a suitable storage
option in high-technology areas (for example, aircraft fuel),
neither method appears very suitable for more mundane
applications. An attractive alternative to conventional methods
is storage as a metal hydride. Such compounds derive their
advantage from the volumetric density of hydrogen in them (which
exceeds that of liquid hydrogen) and the relative ease and safety
with which they can be handled.

Unfortunately, although over 40 elemental metals will react
directly with hydrogen to form a binary metal hydride (a compound
of one metal with hydrogen), all, excepting magnesium hydride,
MgH_2, and vanadium hydride, VH_2, can be eliminated from
consideration for use as a common, hydrogen storage compound.
They are too stable, too unstable, or too expensive. Thus most
attention has been directed toward the use of certain metal alloy
hydrides which are formed by the direct and reversible reaction
of hydrogen with an intermetallic compound. Three well known
intermetallic hydrides which are of interest in this context are
magnesium nickel hydride, Mg_2NiH_4, Lanthanum nickel hydride,
$LaNiH_{6.5}$ and iron titanium hydride, $FeTiH_{1.9}$. Some pertinent
properties of candidate H storage compounds are listed in the
accompanying Tables.

While MgH_2 has by far the greatest storage capacity of the hydrides listed, it is also the most stable and requires a relatively high temperature as well as high heat input to evolve hydrogen at usable pressures. These properties would incur formidable problems which would require expensive solutions in practical storage systems. Mg_2NiH_4 is only a marginal improvement over MgH2 in this respect. By contrast, both $LaNiH_6$ and $FeTiH_{1.9}$ have dissociation pressures in excess of 1 atm at 25°C and have relatively low heats of decomposition. These are important advantages which offset their lower hydrogen content. Indeed, these properties have been decisive, and both $LaNiH_6$ and $FeTiH_{1.9}$ or similar materials have demonstrated their utility as hydrogen (energy) storage media in both stationary and automotive applications.

Table 1: Material Characteristics

Technology	Theoretical H$_2$ yield kg H$_2$/kg materials	Practical Storage cap. kg H$_2$/kg materials	Ah/kg materials	Wh/kg materials (at 0.7V)	Wh/L materials (at 0.7V)	Thermal Burden kJ/kg H$_2$	Required Ancillaries Heat/Cool System Heat Source (Sink) Temperature, °C Source	Sink
FeT$_1$H$_2$ Mn = 105.7	0.0192	0.0175	469	328	1794	16862	~30	<30
LaNi$_5$H$_{6.6}$	0.0152	0.0137	367	257	1671	15062	~40	<40
Mg$_2$Ni$_1$H$_4$	0.037	0.0316	847	593	1524	32217	~280	<280
MgH$_2$	0.076	0.070	1876	1313	1904	38702	~310	<310
VH$_2$	0.022	0.020	536	375	1782	17573	~30	<30

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Table 2: **Mission-Specific Estimates**

Tech.	Est. wt. (kg) for a 300W, 10kWh system, 30 h dis	Est. vol. (L) for a 300 W, 10kWh system, 50% voids	Est. wt. (kg) for a 100W, 1kWh system 10 h dis	Est. vol. (L) for a 100 W, 1kWh system 50% v.	Est. wt. (kg) for a 10W, 90kWh system, 9000 h dis	Est. vol. (L) for a 10 W, 90 kWh system 50% voids
$FeTiH_2$	30.5	11.2	3.05	1.12	274	100
$LaNi_5H_6$	38.91	12.0	3.89	1.20	350	108
$MmNi_5H_6$	39.5	12.0	3.95	1.20	356	108
Mg_2NiH_4	16.9	13.1	1.68	1.31	152	117
MgH_2	7.62	10.5	0.76	1.05	68.5	91

orlando2

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Table 3: Evaluation

Technology	Time to implement Short = 1-3 yrs Medium = 3-5 yrs	Research/Resources	Probability of Success %
FeTi type	Short	Relatively modest	99+
LaNi$_5$ type	Short	Relatively modest	99+
Mg$_2$Ni	Medium	Large	<75
Mg+Mg$_2$Ni	Medium	Large	<50

orland10

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METAL HYDRIDES AS HYDROGEN STORAGE MEDIA

J. J. Reilly

Department of Applied Science
Brookhaven National Laboratory
Upton NY, 11973

Presented at the

Workshop For Hydrogen Storage and Generation Technologies for Medium Power and Energy Applications

April 8-10, 1997

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METAL HYDRIDES

- GAS/SOLID SYSTEMS: ENERGY STORAGE, FUEL CELLS, HEAT ENGINES, HEAT PUMPS

- ELECTRO-CHEMICAL: REPLACEMENT FOR Cd ELECTRODE IN NICAD BATTERIES

- SLURRIES: HYDROGEN RECOVERY, HEAT PUMPS, HYYDROGENATION CATALYSTS

MET-HYD

Hydride	Wt % H	N_H
LiH	12.7	5.9
AlH$_3$	10.1	
CaH$_2$	4.2	5.1
MgH$_2$	7.6	6.6
NaH	4.8	5.1
TiH$_2$	4.0	9.1
ZrH$_2$	2.2	7.3
LaH$_3$	2.1	6.8
UH$_3$	1.3	8.4
H$_2$ Liquid	100	4.2

$N_H \times 10^{22}$ = number of H atoms/cm^3

$$M + X/2H_2 \underset{\text{HEAT ABSORBED}}{\overset{\text{HEAT RELEASED}}{\rightleftharpoons}} MH_X$$
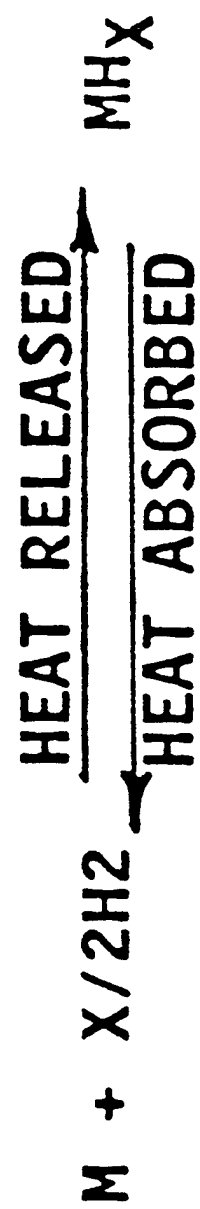
HYDRIDE	HEAT OF FORMATION
	KCAL
LiH	-21.7
CaH$_2$	-41.6
MgH$_2$	-18.5
TiH$_2$	-29.9
ZrH$_2$	-39.7
UH$_3$	-30.8
LaH$_2$	-49.7

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HYDROGEN CONTENT OF VARIOUS STORAGE MEDIA

ALLOY CLASS	HYDRIDE	% BY WEIGHT	GRAMS H/ml
A	MgH_2	7.7	0.101
A2B	Mg_2NiH_4	3.6	0.081
AB2	$TiCr_{1.8}H_{3.6}$	2.5	0.09
AB	$FeTiH_2$	1.9	0.096
AB5	$LaNi_5H_6$	1.4	0.089
LIQUID H_2		100	0.07
H_2 100 atm		100	0.008

DC_TABLE

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HYDROGEN CONTENT OF VARIOUS STORAGE MEDIA

HYDRIDE	ΔH_f/mol H_2 kJ	H storage cap. % by weight	Ah/kg @0.7V	Wh/L @0.7V
MgH_2	-81.0	7.0	1313	1904
Mg_2NiH_4	-64.2	3.16	593	1524
$TiCr_{1.8}H_{3.6}$	-20	2.5	469	≈1600
VH_2	-41	2.0	375	1782
$FeTiH_2$	-31(avg.)	1.75	328	1794
$LaNi_5H_6$	-33	1.37	257	1671
LIQUID H_2		100	18760	1313
H_2 100 atm		100	18760	188

or:lando7

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lnP$_{plateau}$

1/T

FIGURE 1-1-B

P$_{eq}$

H CONTENT

FIGURE 1-1 A

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chap1
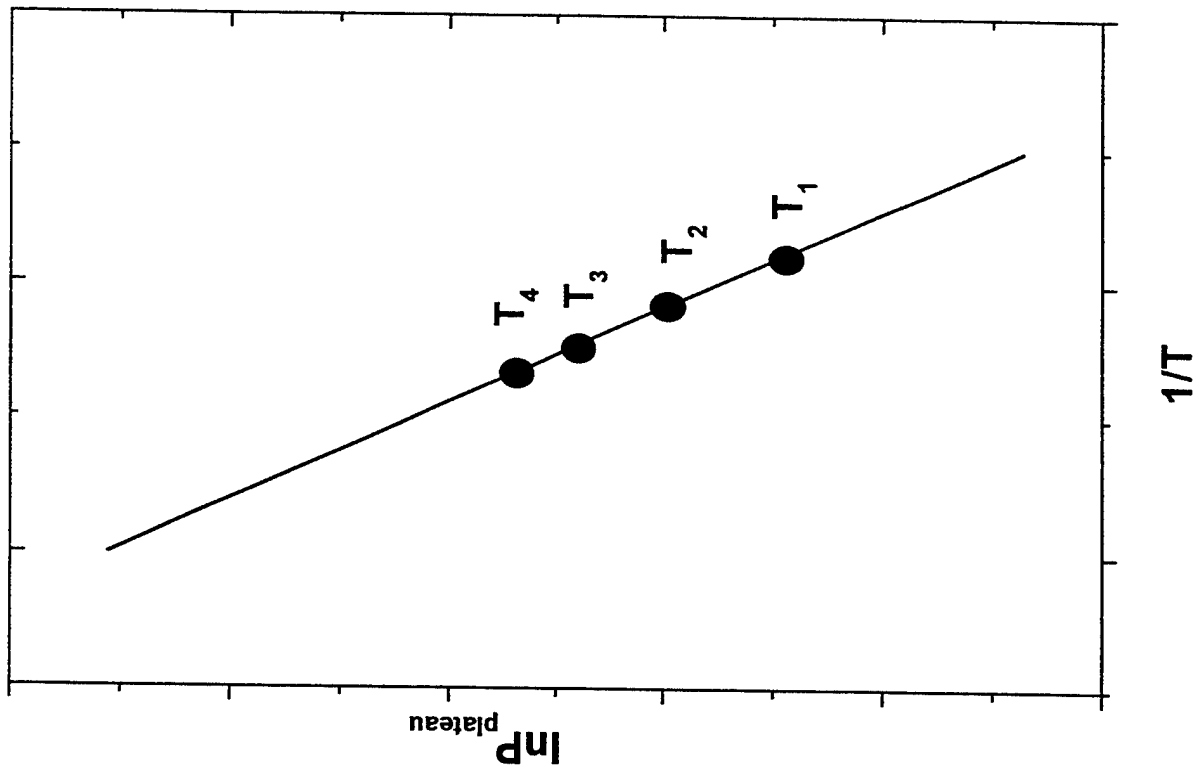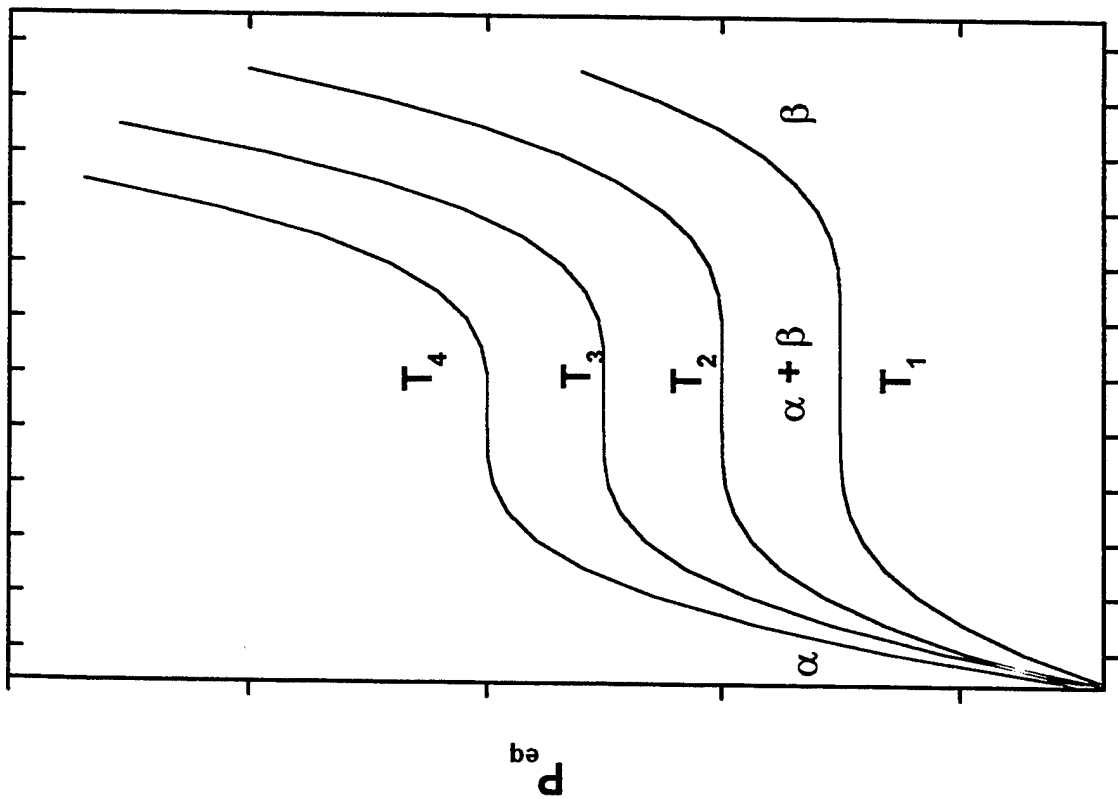
SEQUENCE OF ELEMENTARY STEPS

- PRODUCTION OF H* ON ALLOY SURFACE (CHEMICALLY OR ELECTROCHEMICALLY).

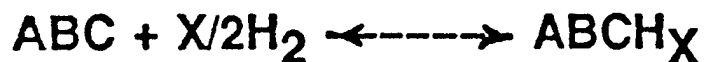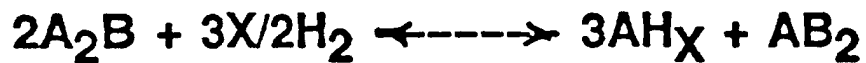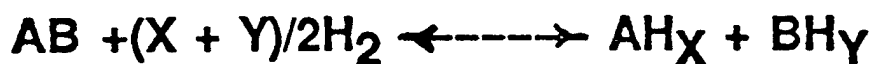- H DIFFUSION INTO SUBSURFACE β PHASE.

- $\alpha \rightarrow \beta$ CONVERSION AT β/α INTERFACE.

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LaNi$_5$ Reaction Pathway
Hydride Formation/Decomposition
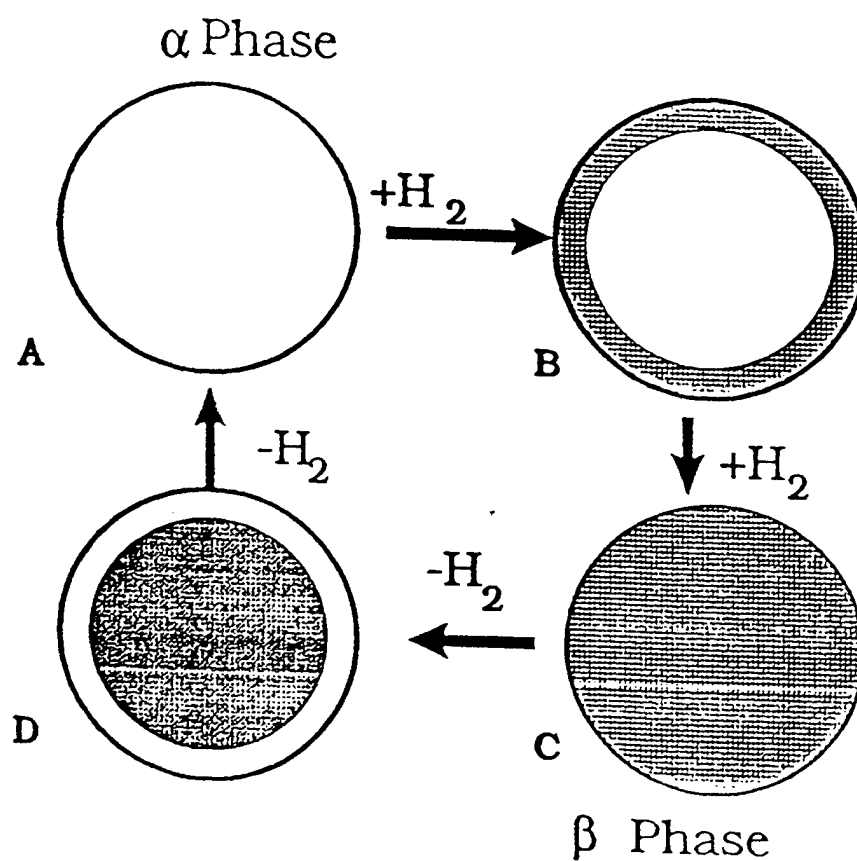
POSSIBLE ALLOY/H REACTIONS

$AB + X/2H_2 \longleftrightarrow AH_X + B$

$AB + X/2H_2 \longleftrightarrow ABH_X$

$3AB + X/2H_2 \longleftrightarrow A2BH_X + AB_2$

$AB + (X + Y)/2H_2 \longleftrightarrow AH_X + BH_Y$

$A_2B + X/2H_2 \longleftrightarrow A_2BH_X$

$2A_2B + 3X/2H_2 \longleftrightarrow 3AH_X + AB_2$

$ABC + X/2H_2 \longleftrightarrow ABCH_X$

Fe-Ti

WEIGHT % Ti

Fe 10 20 30 40 50 60 70 80 90 Ti

Fe$_2$Ti

FeTi

1670

1536

LIQ.

1427

LIQ.

1289

1317

10 16

35.2

27.6

49.7

1085

79

52.5

70.5

(β-Ti)

(δ-Fe)

FeTi
+
(β-Ti)

882

(α-Fe)
+
Fe$_2$Ti

Fe$_2$Ti
+
FeTi

590

86

FeTi
+
(α-Ti)

TEMPERATURE, °C

2000
1600
1200
800
400
0
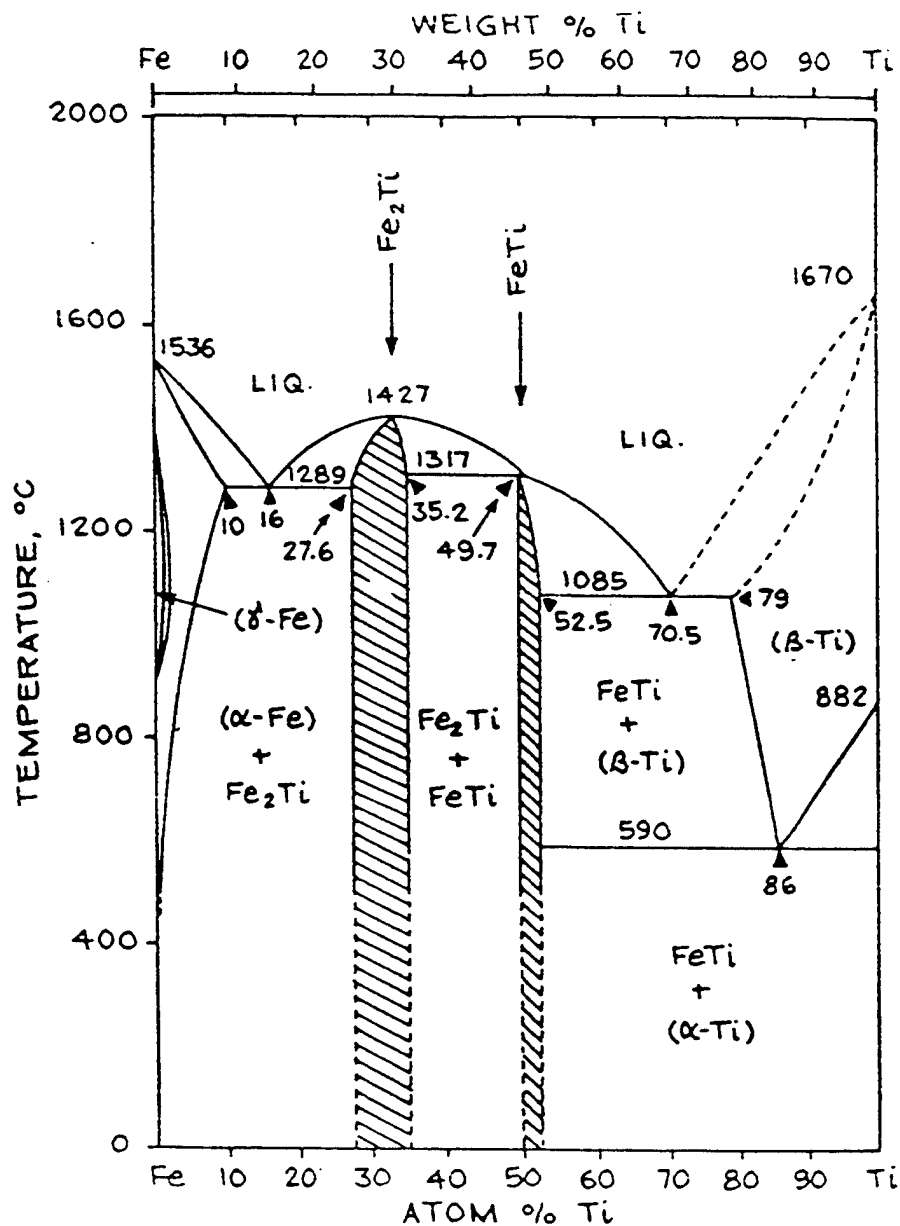
Fe 10 20 30 40 50 60 70 80 90 Ti
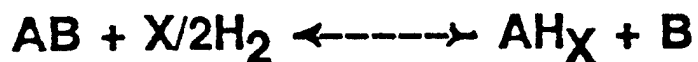
ATOM % Ti

Diagram redrawn from ref. 1 which reviews data through 1980.
This ref. contains information on crystal structures, lattice
parameters, thermodynamics and metastable phases, and should
be consulted if detailed information is required.

(1) Murray, J.L.
    "The Fe-Ti (Iron-Titanium) System."
    BULL. ALLOY PHASE DIAGR.; 2, (3), (1981); pp 320-334

300

$FeTi + 1/2H_2 \leftrightarrow FeTiH$

$\Delta H_{298} = -28 \text{ kJ/mol } H_2$

$\Delta G_{298} = 3.5 \text{ kJ/mol } H_2$

$FeTiH + 1/2 H_2 \leftrightarrow FeTiH_2$

$\Delta H_{298} = -33.3 \text{ kJ/mol } H_2$

$\Delta G_{298} = 5.7 \text{ kJ/mol } H_2$

orlando4

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FeTi + H₂ ⇌ FeTiH₂

313K

Figure 6
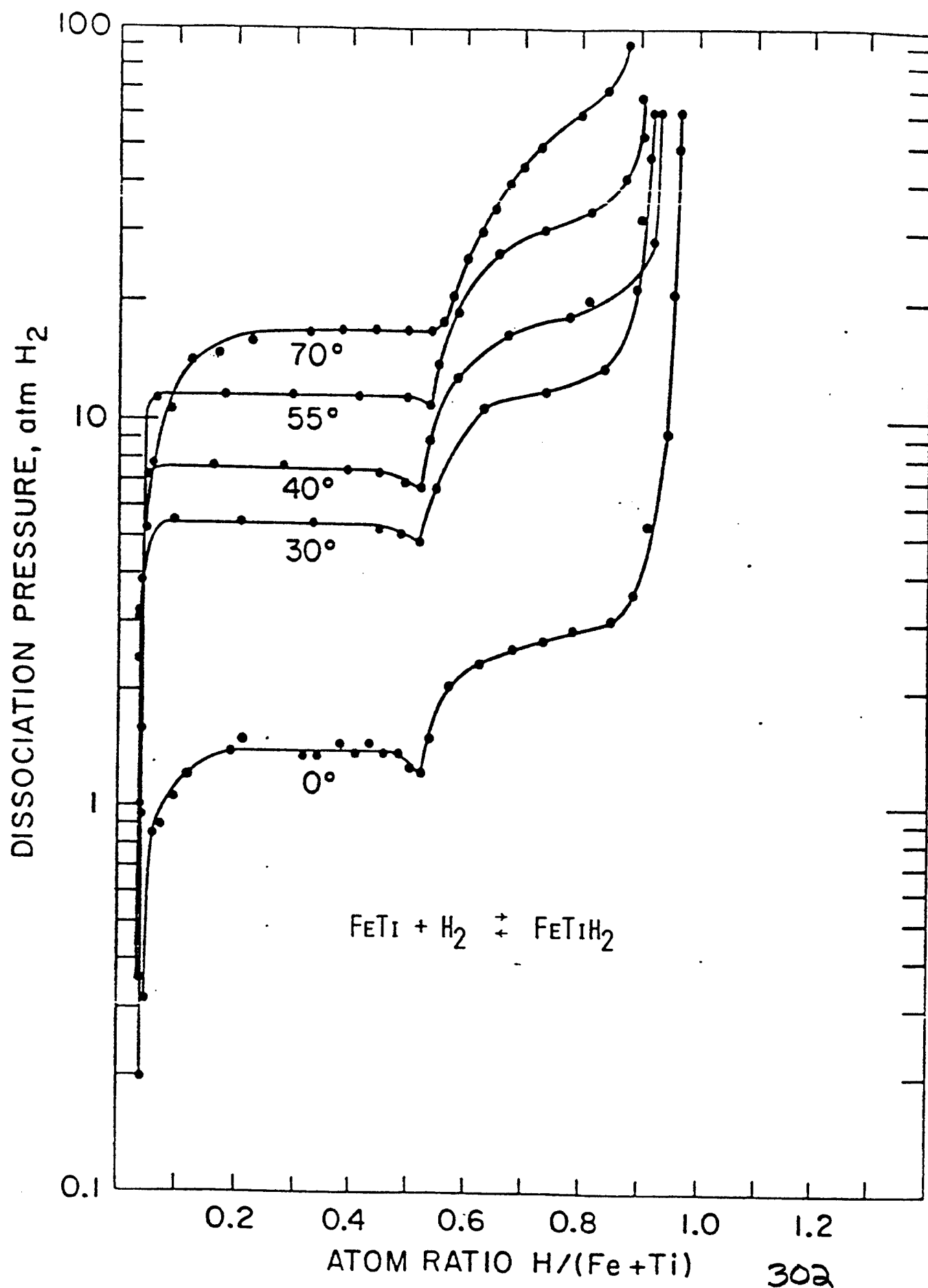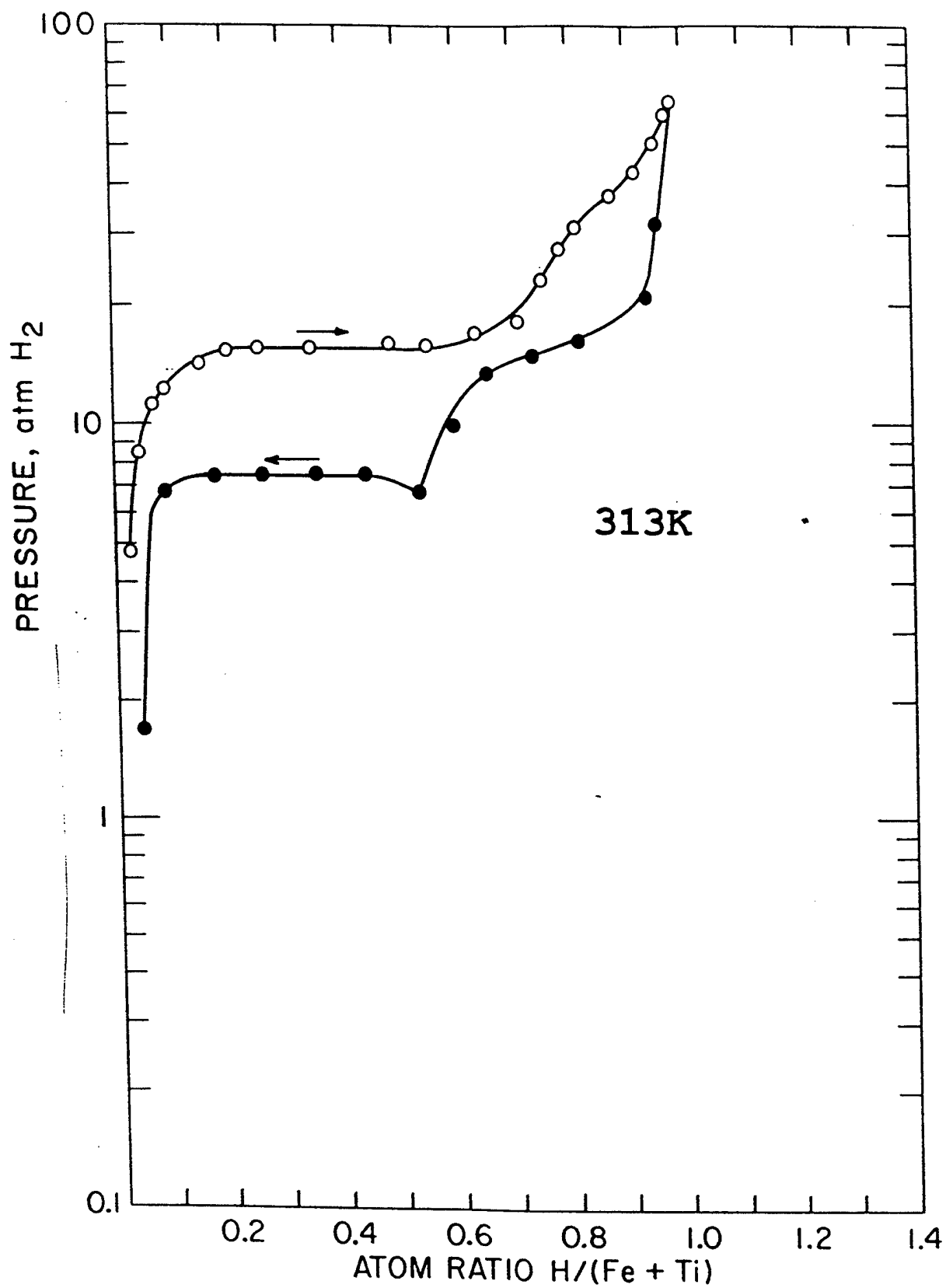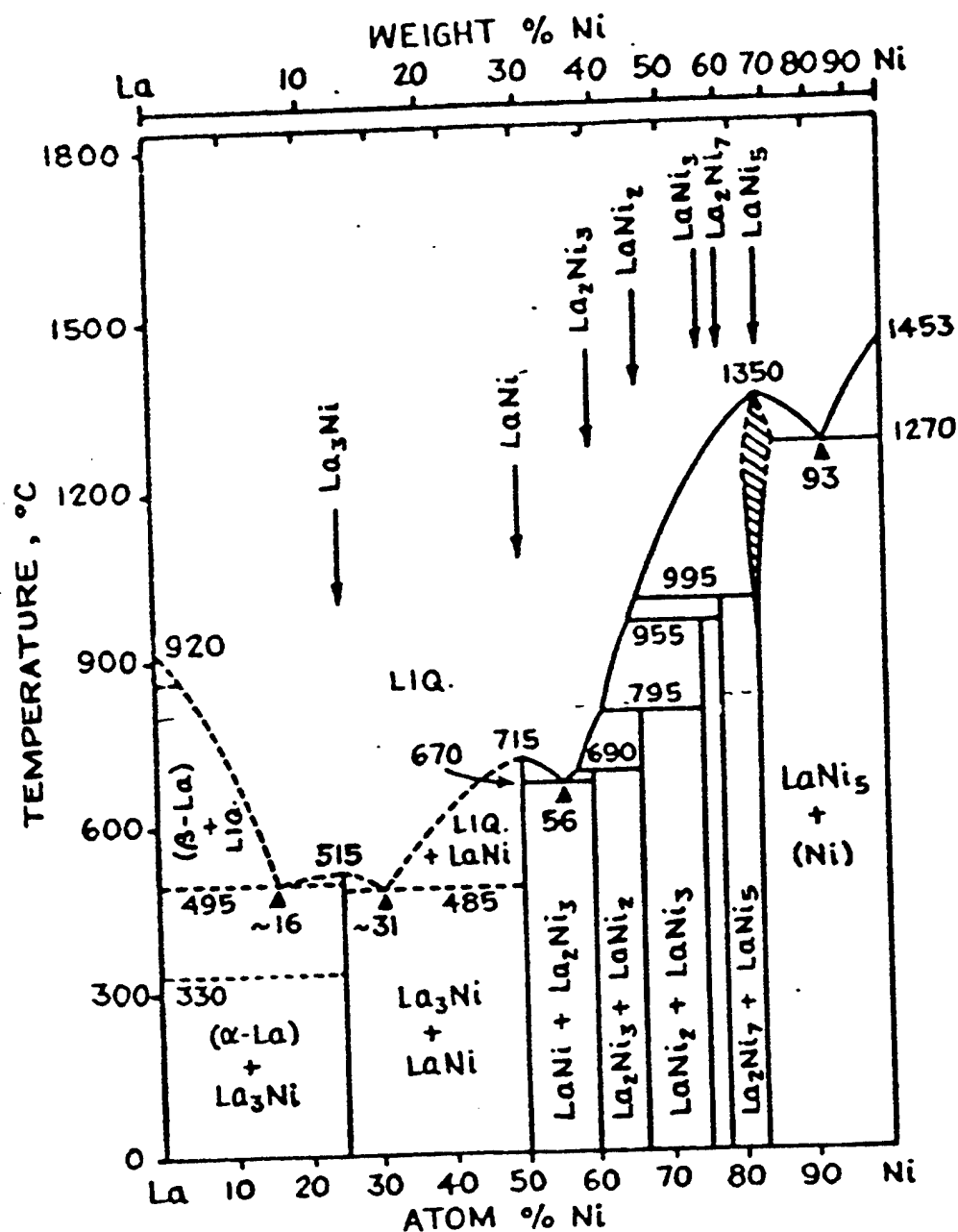
La·Ni

Portion 0-50 at. pct Ni, Hansen Fig. 488 except for MP of La
from Elliott Table A and MP of LaNi, ref. (1). Portion 50-100
at. pct Ni, ref. (1), except LaNi1.4 of ref. (1) was later shown
to be La2Ni3, ref. (2).

(1) Buschow, K.H.J. and Van Mal, H.H.
    "Phase Relations and Hydrogen Absorption in the Lanthanum-
    Nickel System."
    JLCM; 29 (1972); pp 203-210

(2) Van Vucht, J.H.N. and Buschow, K.H.J.
    "The Crystal Structure of La2Ni3."
    JLCM; 46 (1976); pp 133-138

6/80   304

$$LaNi_5 + 3H_2 \leftrightarrow LaNi_5H_6$$
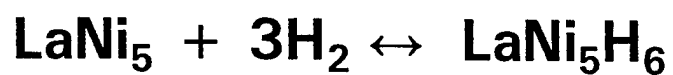
$$\Delta H_{298} = -33 \text{ kJ/mol } H_2$$

$$\Delta G_{298} = 0 \text{ kJ/mol } H_2$$

$$LaNi_5 + H_2 \leftrightarrow LaH_2 + Ni$$
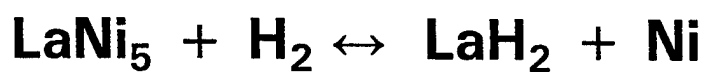
$$\Delta H_{298} = -142 \text{ kJ/mol H2}$$

$$\Delta G_{298} = -100 \text{ kJ/mol H2}$$

LaNi$_5$ + 3H$_3$ $\rightleftharpoons$ LaNi$_5$H$_6$

DISSOCIATION PRESSURE (atm)

HYDROGEN CONCENTRATION (AT H mol LaNi$_5$

140°C

120°C

100°C

60°C

40°C

20°C

306

307
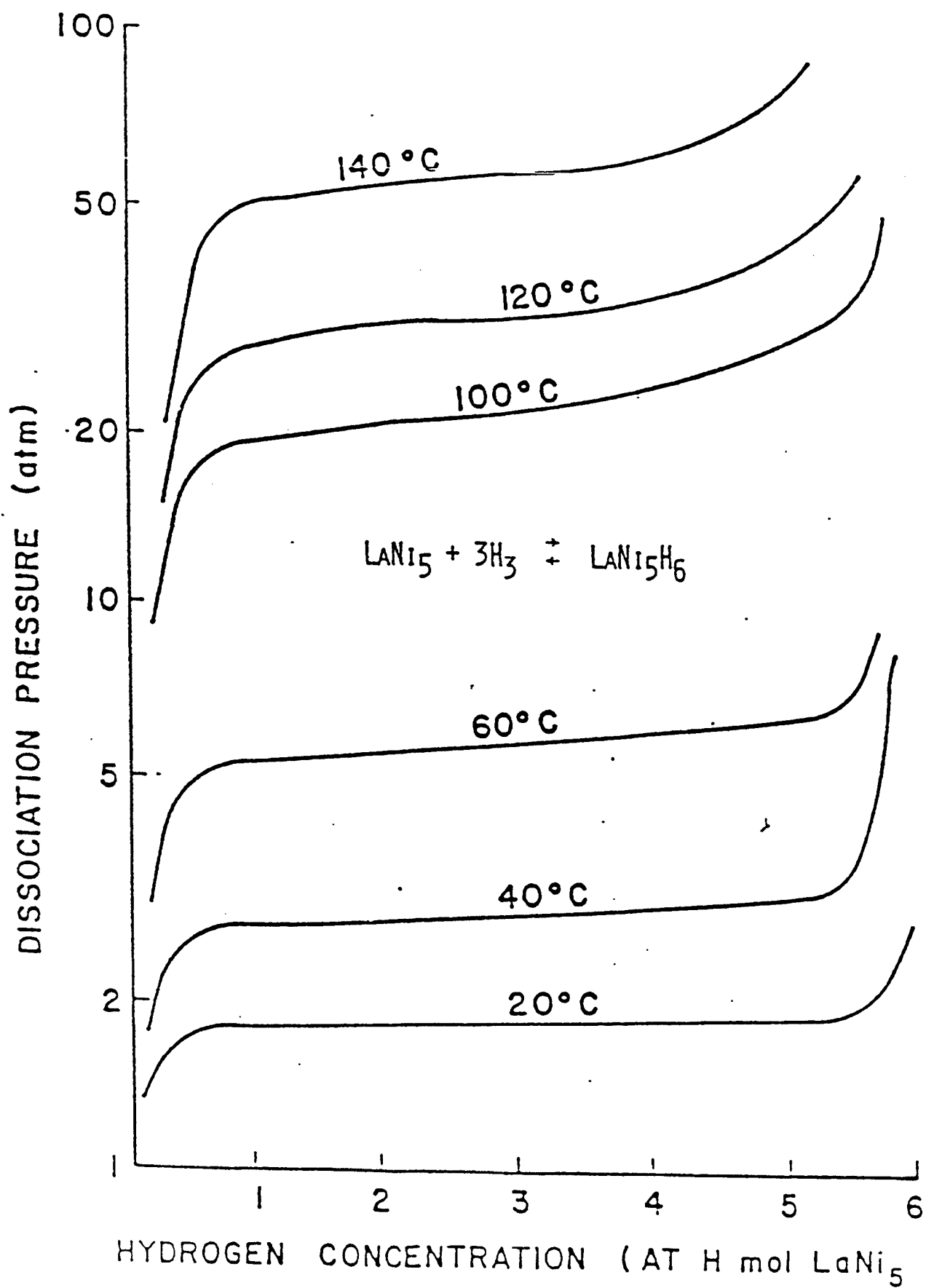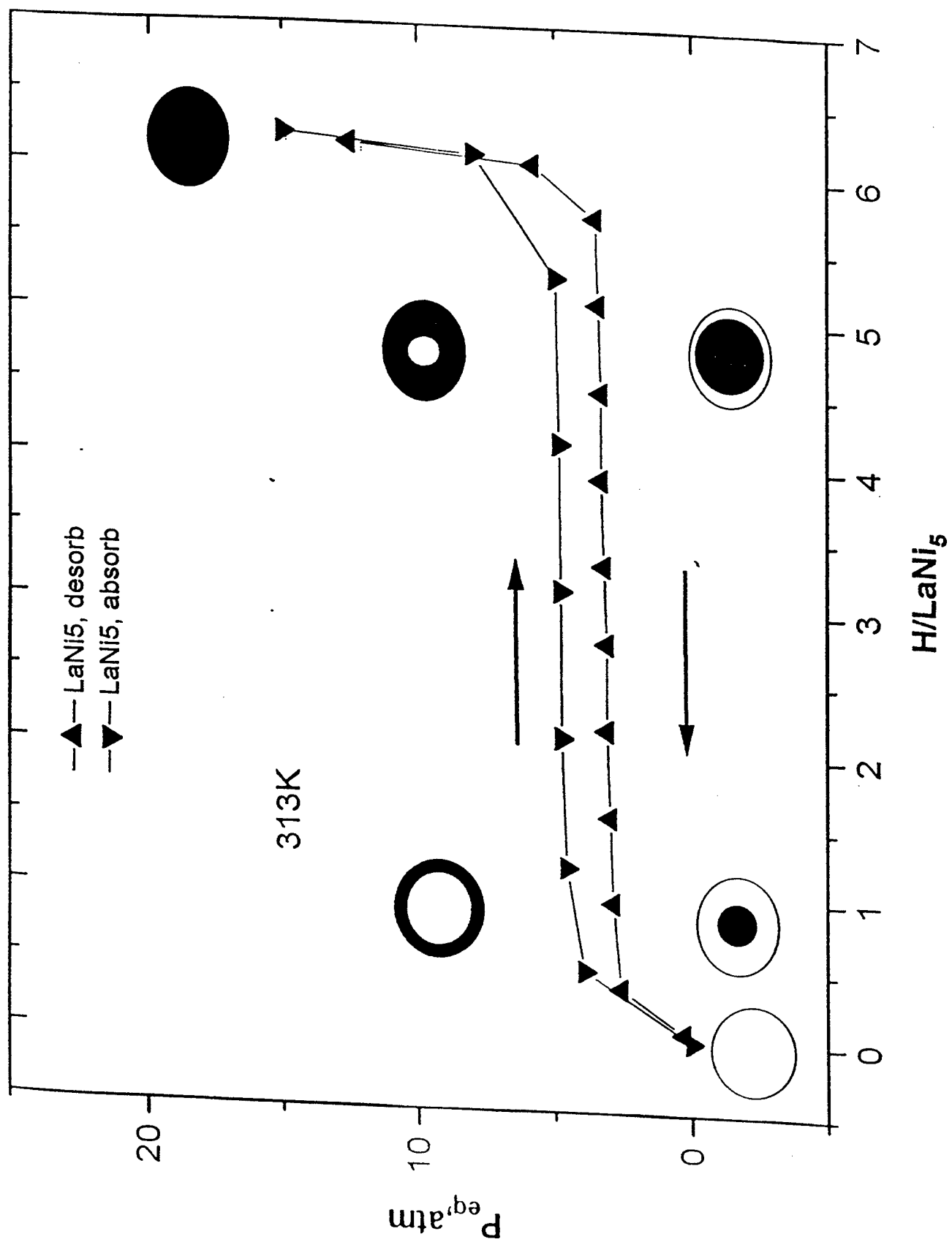
MOLAR VOLUME (V$_H$) OF HYDROGEN AB$_5$ HYDRIDE

LaNi$_5$ + 3H$_2$ → LaNi$_5$H$_6$

86.06 Å^3 → 107.06 Å^3

EXPANSION OF UNIT CELL = 21 Å^3

V$_H$ = 3.5 Å^3

LaNi5 CRYSTAL STRUCTURE
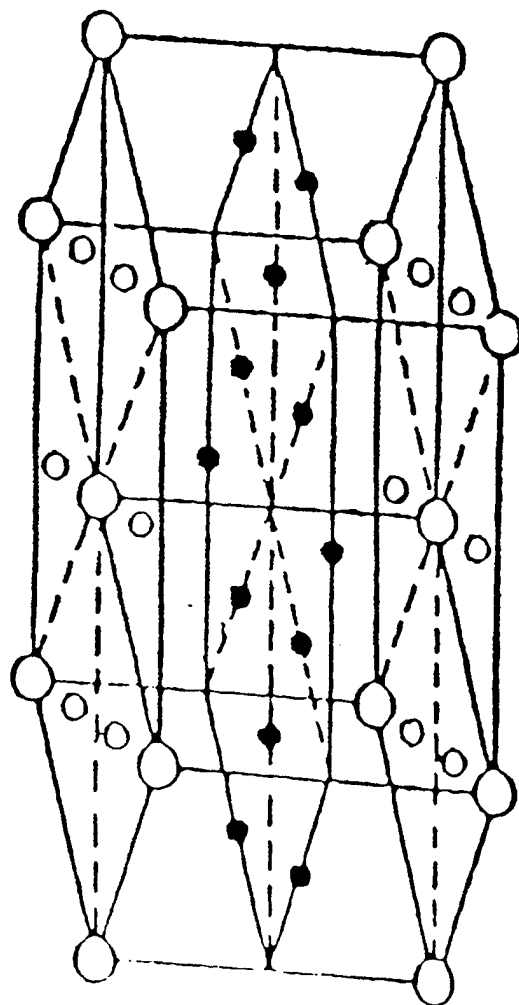
○ Lanthanum 1(a)

○ Nickel Ni_I 2(c)

● Nickel Ni_{II} 3(g)

2 Mg$_2$Cu + 3 H$_2$ $\Leftrightarrow$ 3 MgH$_2$ + MgCu$_2$

ΔH_{298} = -17.4 kcal/mol H$_2$ = 52.2 kcal

ΔG_{298} = -7.3 kcal/mol H$_2$ = 21.9 kcal

ΔH_{562} = +1.6 kcal/mol H$_2$ = 4.8 kcal

Mg$_2$Cu + 2 H$_2$ $\Leftrightarrow$ 2 MgH$_2$ + Cu
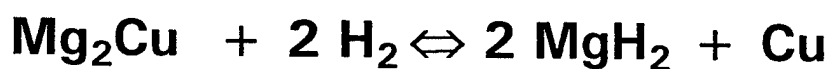
ΔG_{298} = -5.5 kcal/mol H2 = -11.0 kcal

ΔG_{562} = +3.2 kcal/mol H2 = 6.4 kcal

atom	site occ.
La	1
Ni(1,2)	1
Ni(3)	1
D (1)	1/3
D (2)	2/3
D (3)	1/3
D (4)	2/3
D (5)	1

311

FIGURE 2-2-1-5

$$\ln P = -1.8678(vol) + 94.2180$$

Data points (labeled): GdNi5, SmNi5, YCo5, NdNi5, PrNi5, SmCo5, LaNi5, NdCo5, PrCo5, LaNi4.6Al.4, LaCo5

x-axis: Cell Volume, Å

y-axis: $\ln P_{plateau}$ (atm)

CHAP4

Desorption Isotherms at 40°C
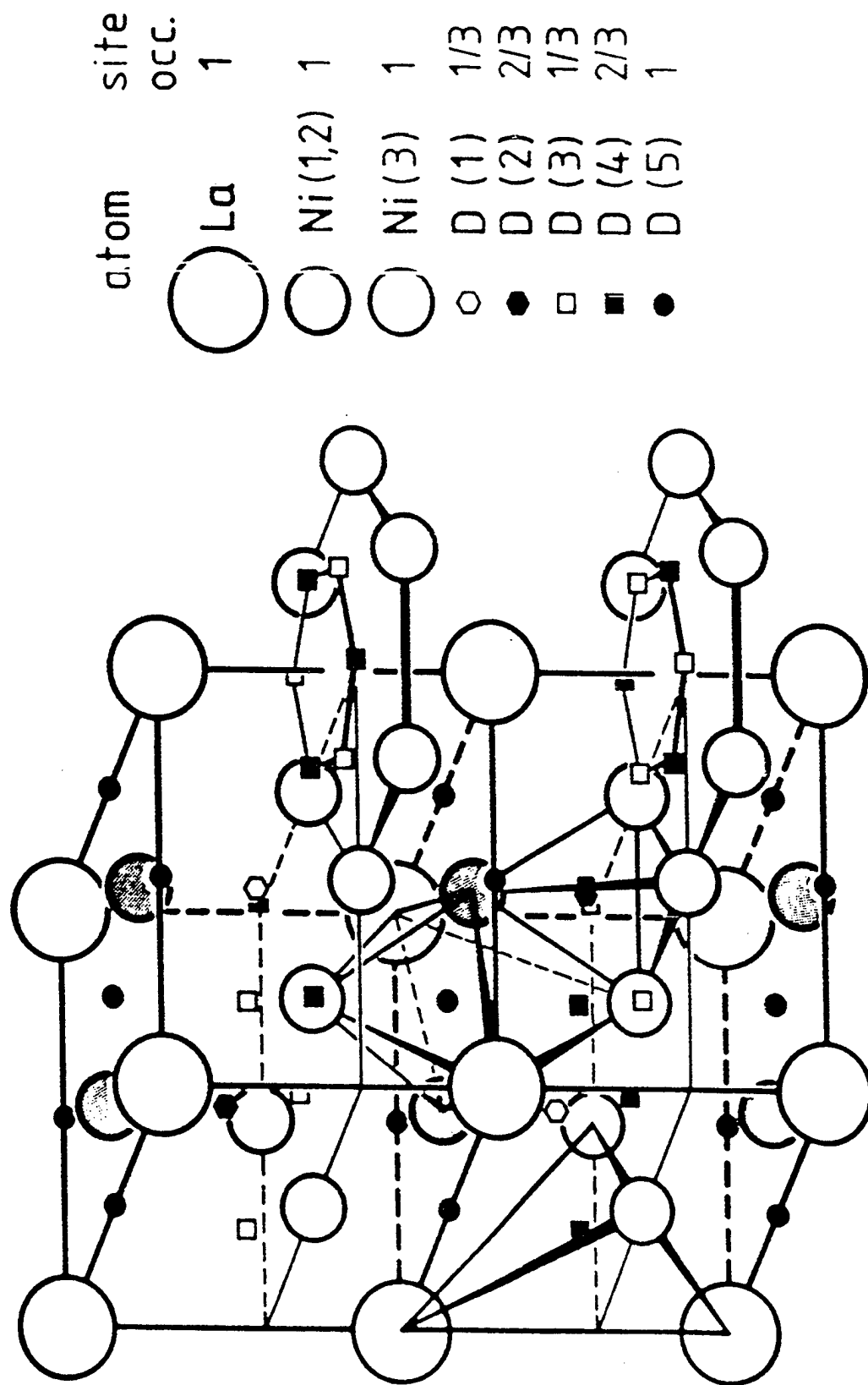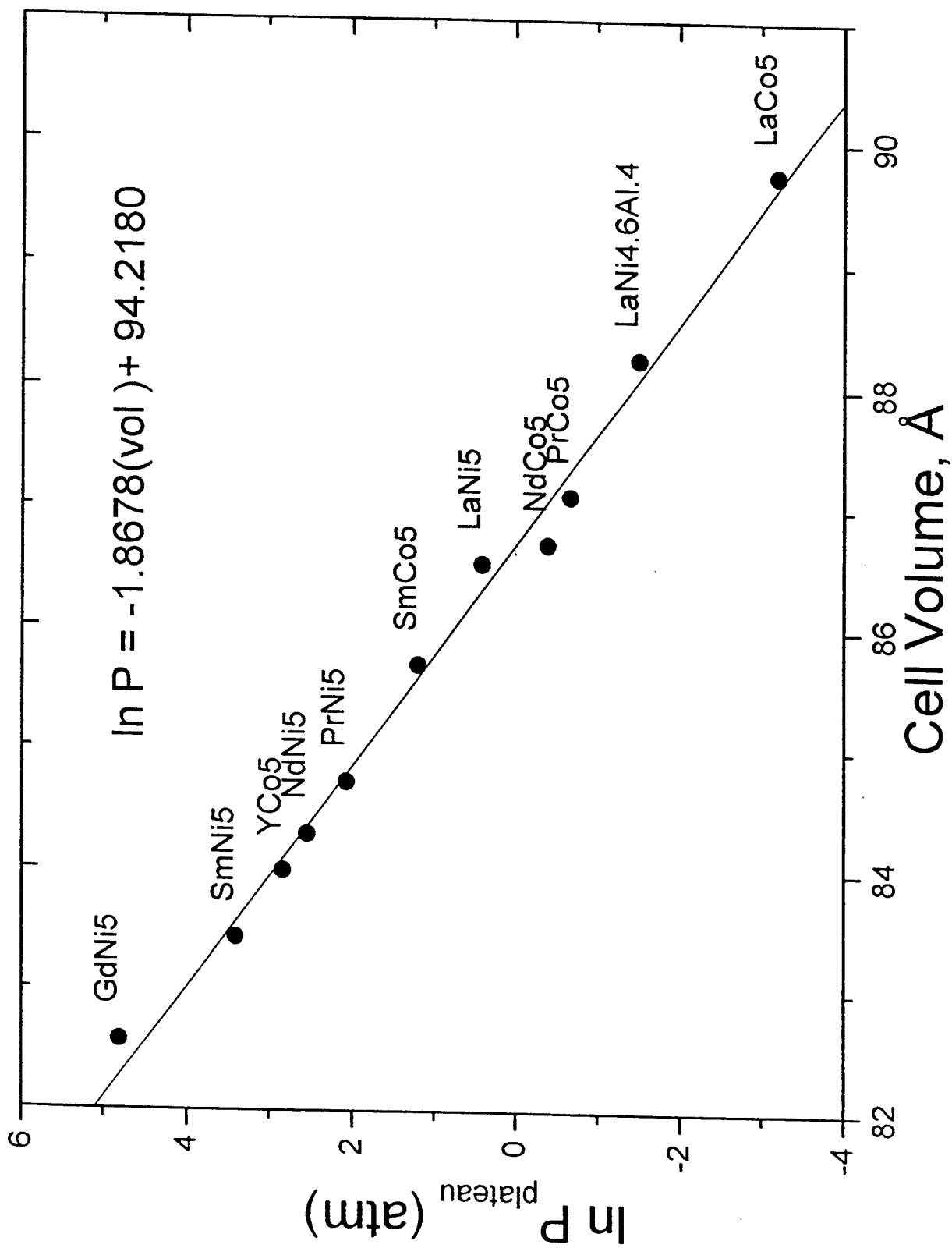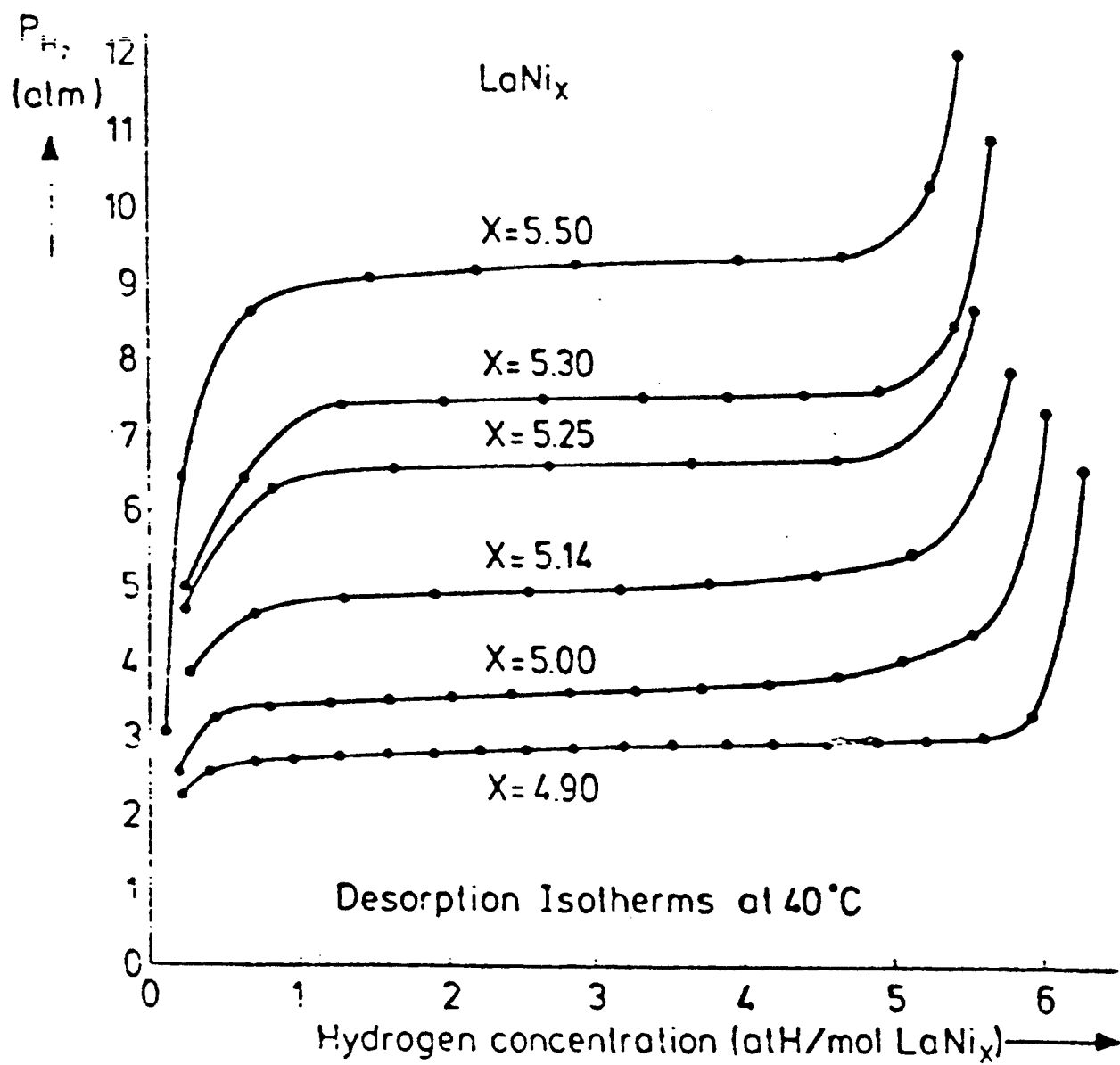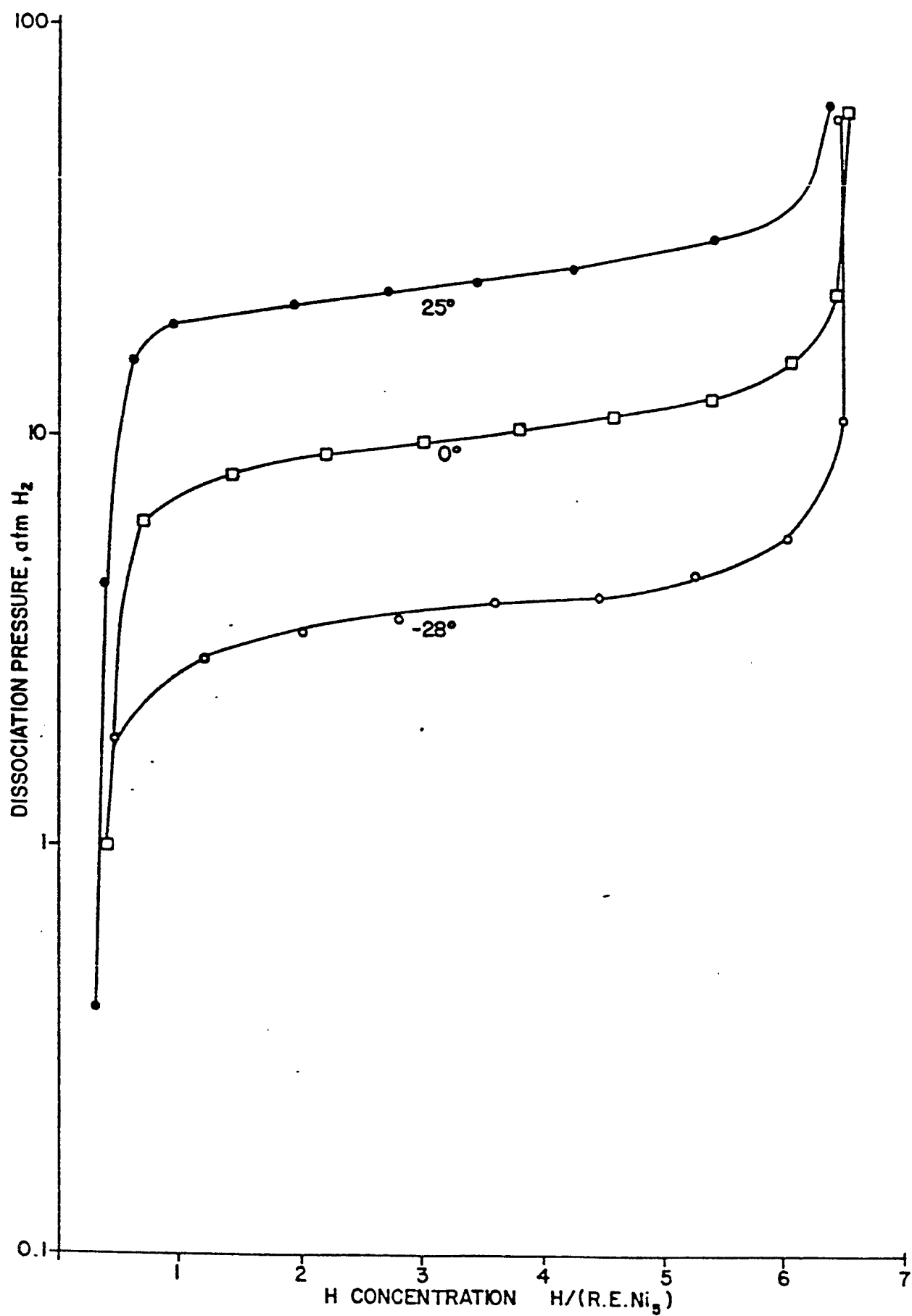
Mg-Ni
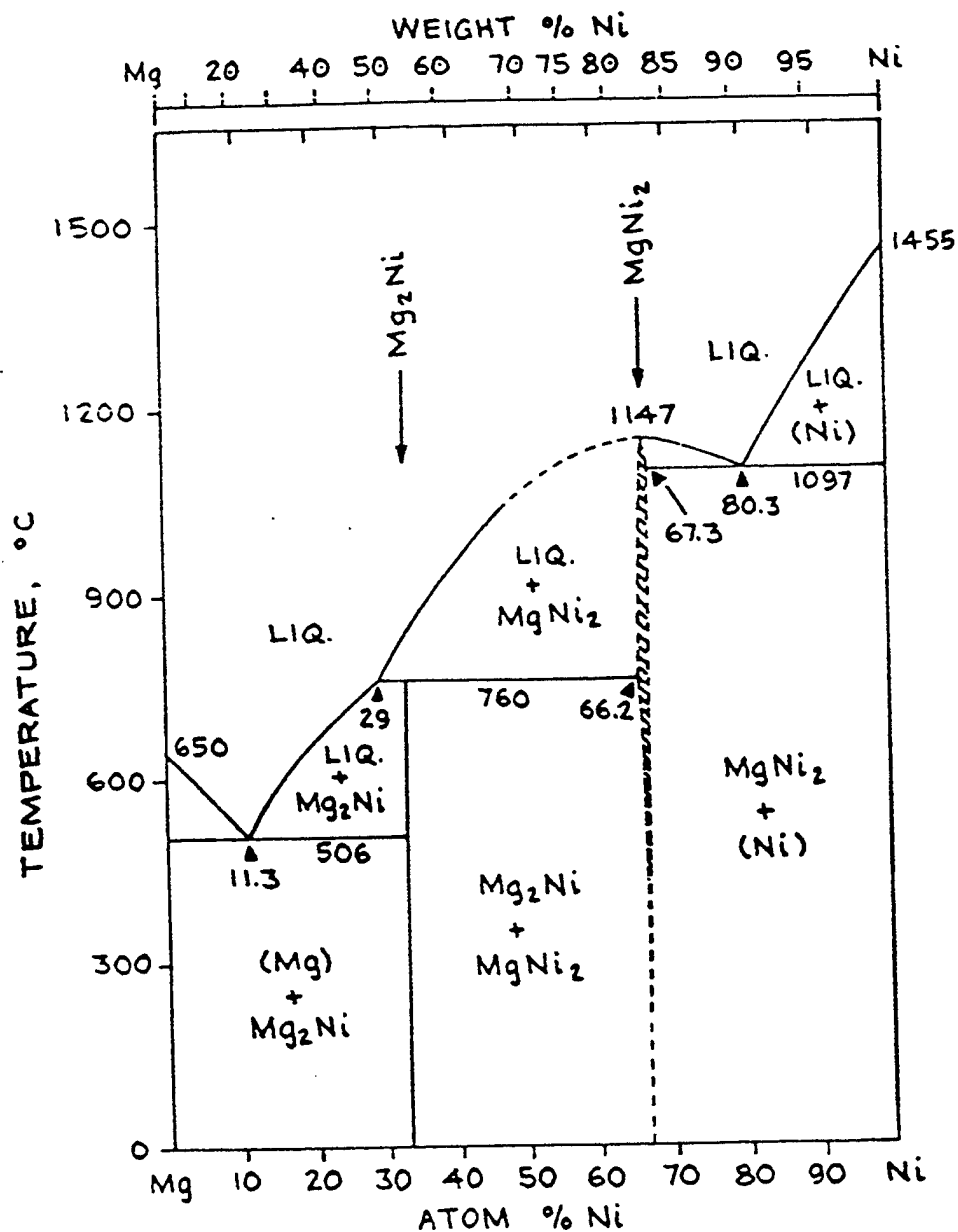
The diagram, redrawn from ref. 1 which reviewed the literature
through 1983, is largely that of Hansen Fig. 503 with minor
modifications. See ref. 1 for information on crystal structure,
thermodynamics, metastable phases and magnetic characteristics.

(1) Nayeb-Hashemi, A.A. and Clark, J.B.
    "The Mg-Ni (Magnesium-Nickel) System."
    BULL. ALLOY PHASE DIAGRAMS; 6(3), 1985; pp 238-244.

8/85

$$Mg_2Ni + 2H_2 \leftrightarrow Mg_2NiH_{4.0}$$
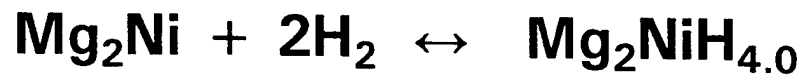
$$\Delta H_{298} = -64.2 \text{ kJ/mol H2}$$

$$\Delta G_{298} = -27.9 \text{ kJ/mol H2}$$

$$\Delta G_{562} = +1 \text{ kJ/mol H2}$$

$$2\ Mg_2Ni + 3\ H_2 \leftrightarrow 3\ MgH_2 + MgNi_2$$
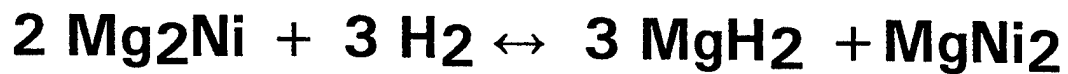
$$\Delta G_{298} = -27.9 \text{ kJ/mol H2}$$

$$\Delta G_{562} = +9.0 \text{ kJ/mol H2}$$

$$Mg_2Ni + 2H_2 \rightleftarrows Mg_2NiH_4$$

349 °C

322 °C

298 °C

317

Figure showing dissociation pressure (ATM H_2) versus composition $H/(Mg + Ni)$ for $Mg_2Ni + Mg$ (70 wt % Mg, 30 wt % Ni) at 324 °C, illustrating the reactions $Mg + H_2 \rightleftharpoons MgH_2$ and $Mg_2Ni + 2H_2 \rightleftharpoons Mg_2NiH_4$.

ELECTROLYTIC CELL

COMPRESSOR

FETiH$_x$ RESERVOIR

FUEL CELL

H$_2$

H$_2$

H$_2$O

AIR
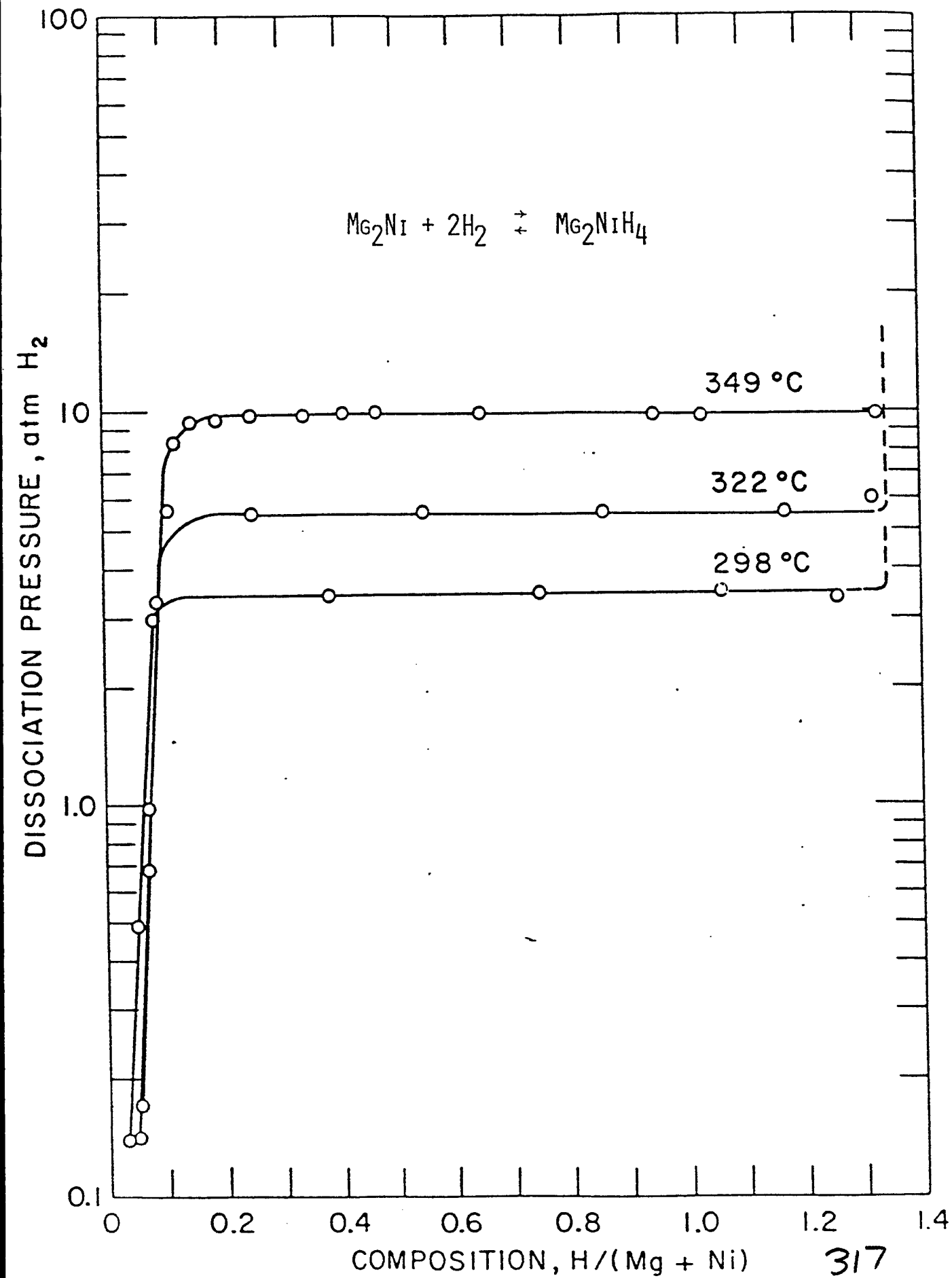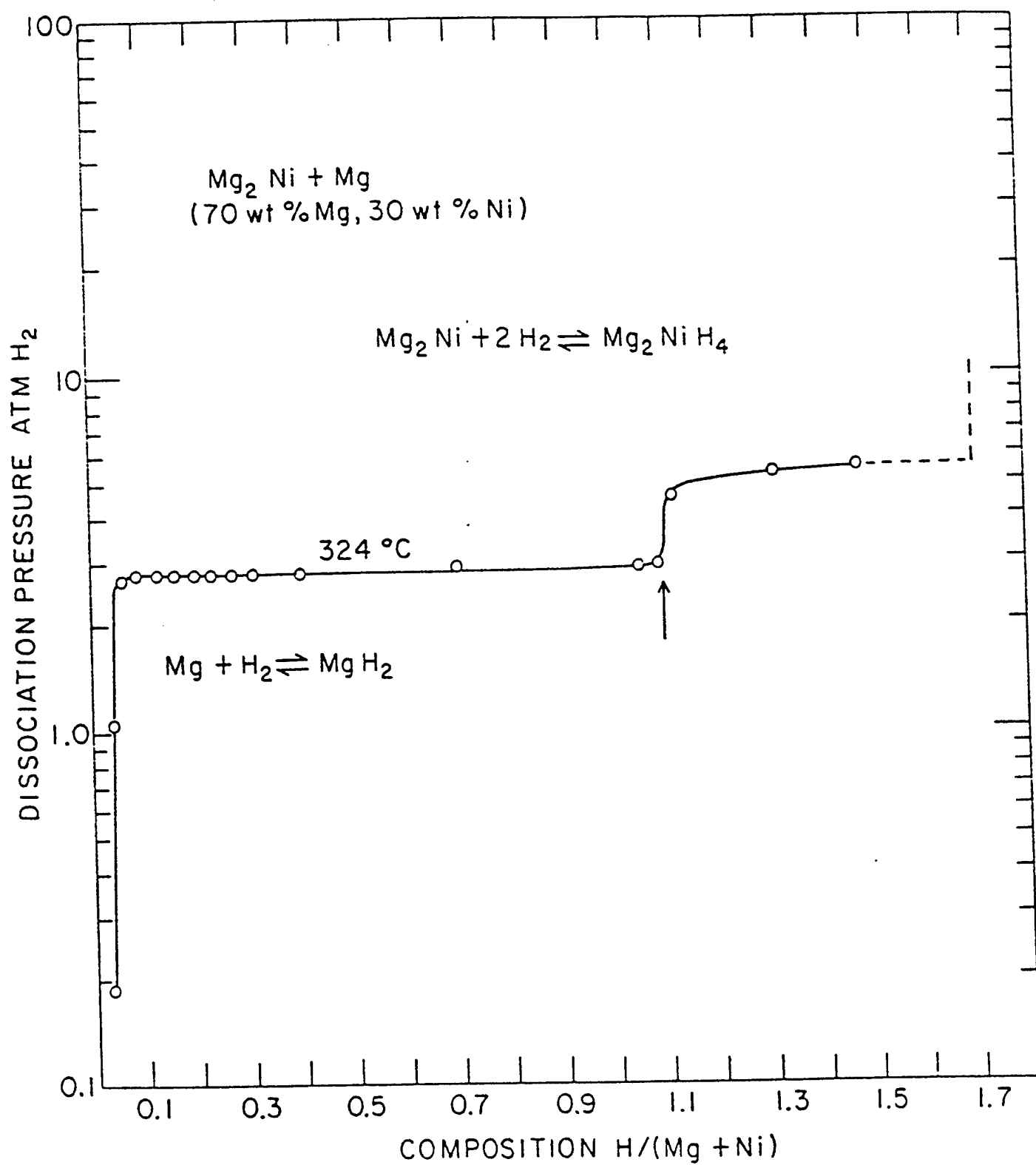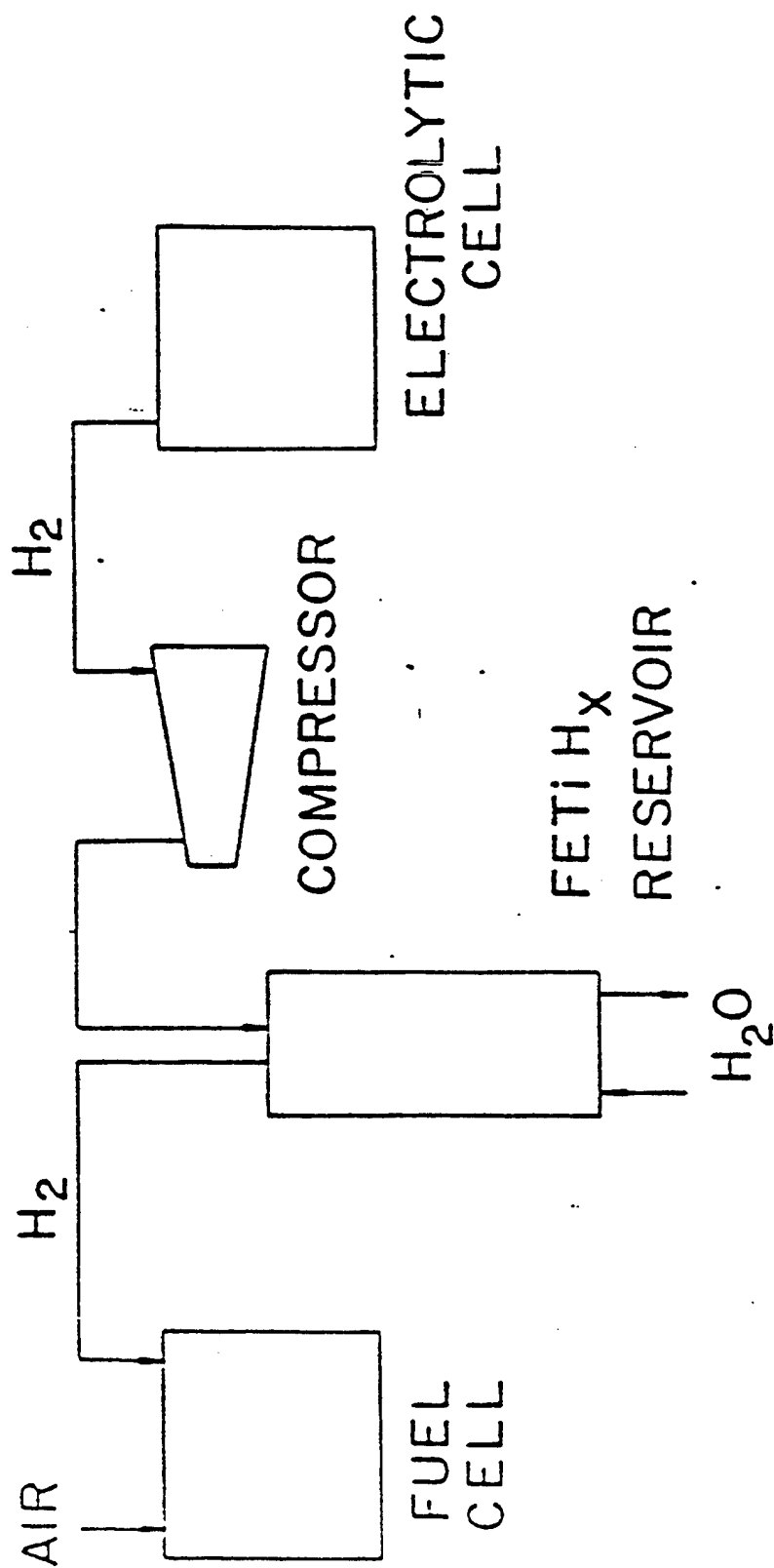
PSE + G PEAK SHAVING DEMONSTRATION

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AIR

ENERGY CONVERTER

H_2

HEAT EXCHANGER

$Fe\,Ti\,H_{\sim 2}$ RESEVOIR

CONVERTER COOLANT LOOP

320

FLOW RATE scfm

8.0 | 3.2

TOTAL H$_2$ DISCHARGED = 13.4 lbs

OVERNIGHT INTERRUPTION

RESERVOIR PRESSURE, psia

AVERAGE BED TEMPERATURE, °C

ELAPSED TIME, hrs
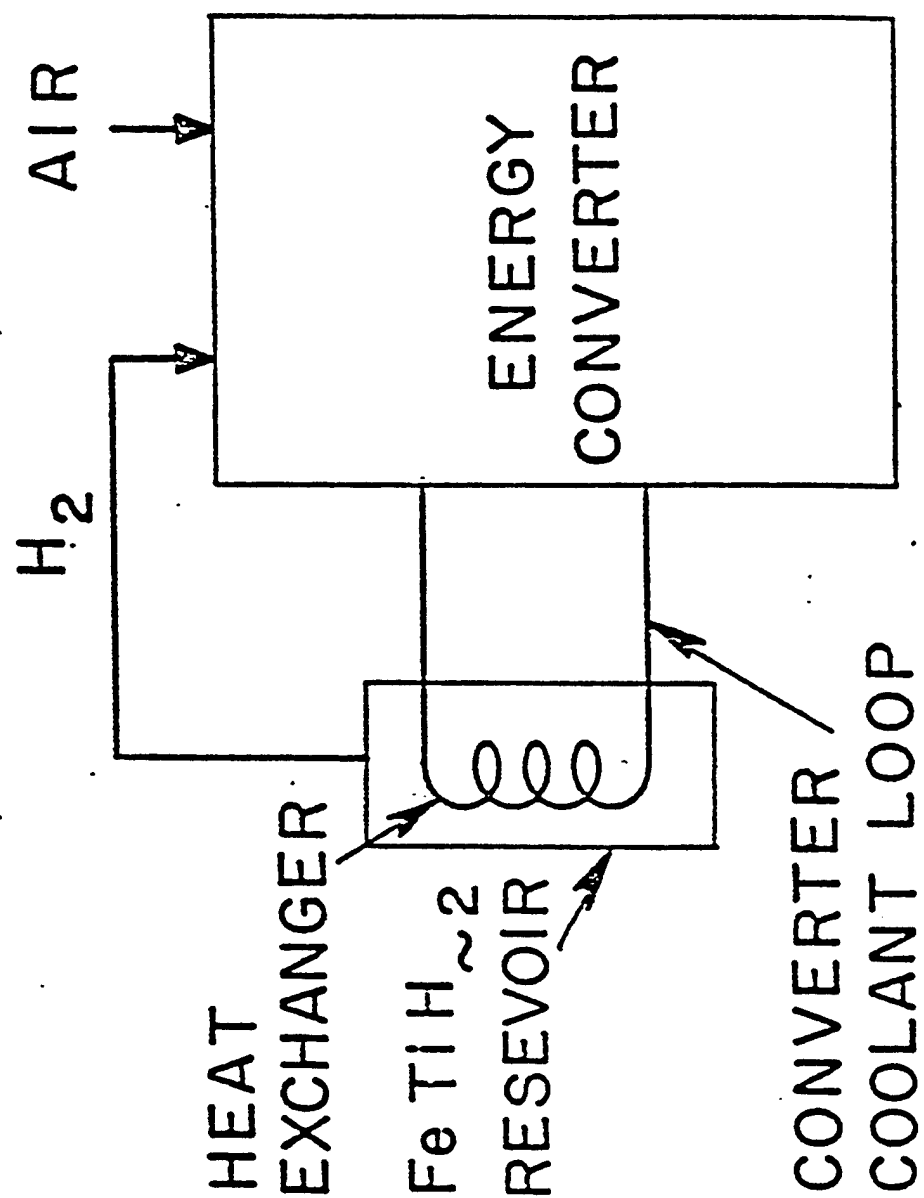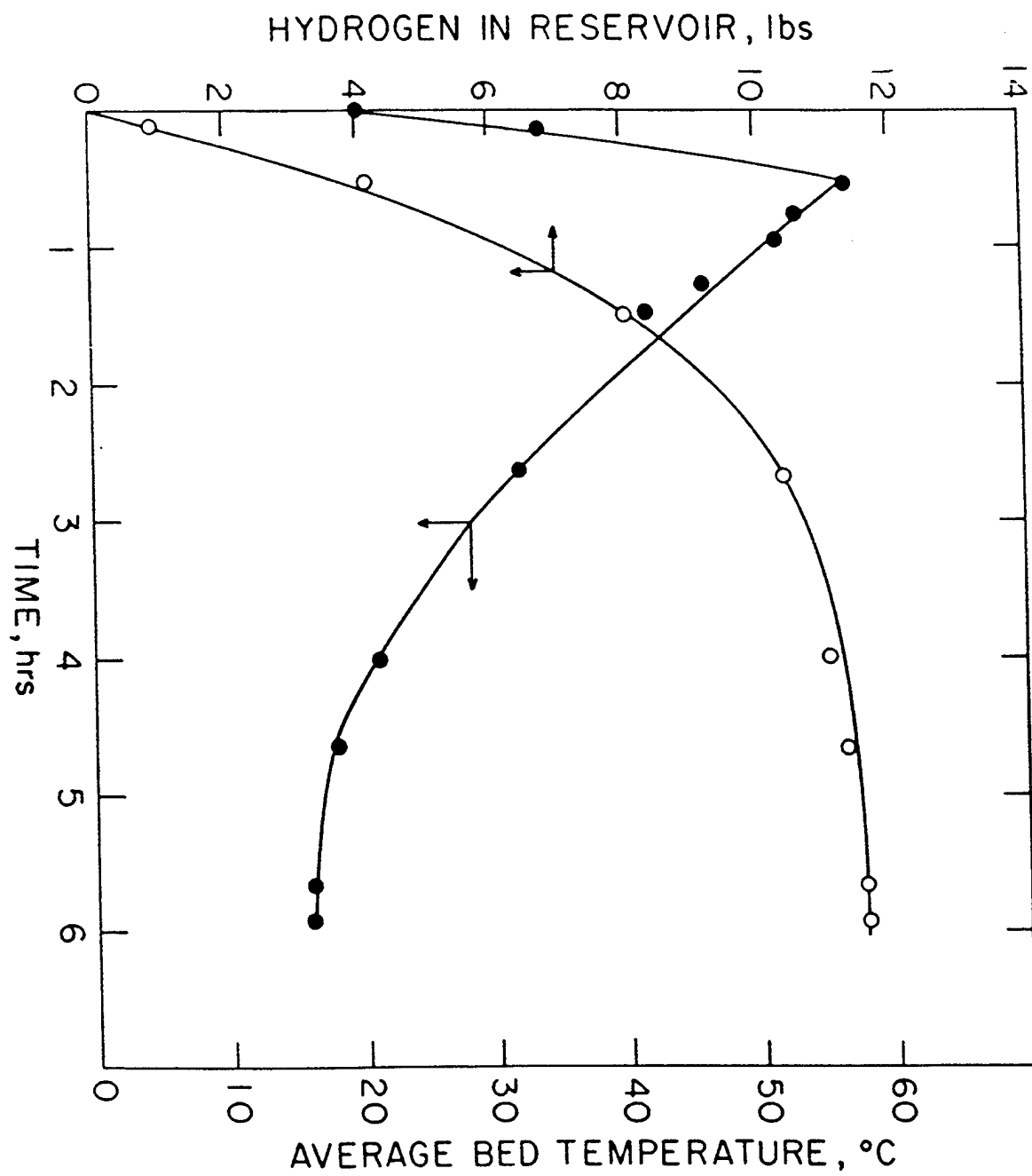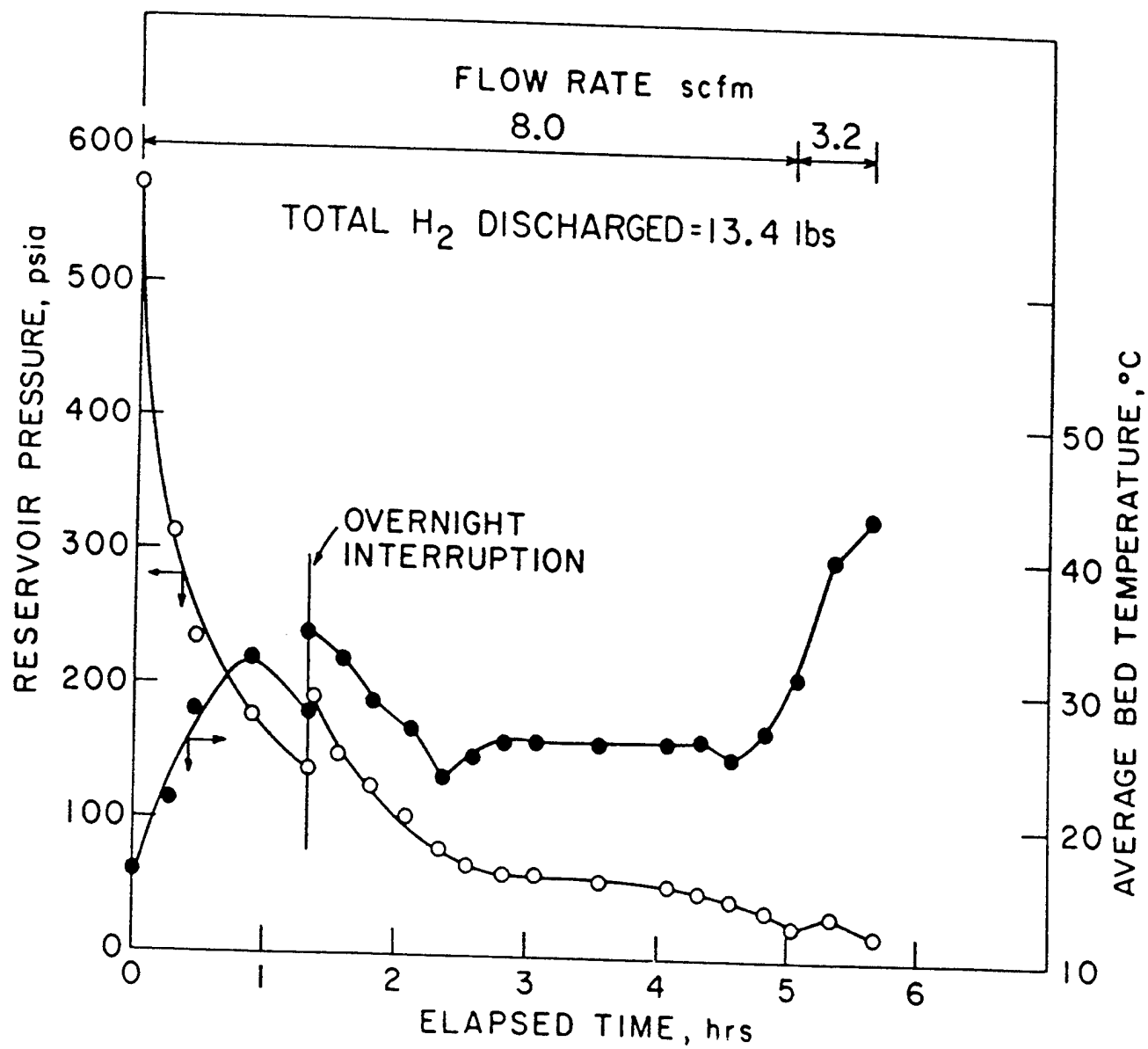
PSE&G FeTiH$_x$ RESERVOIR

kg Alloy	400
Total Ah	1.7E5
Total Wh @ 0.7V	1.2E5
Wh/L of Res. V.@.7V	826
Charge Rate	2.4E4 Ah/h
Discharge rate	3.5E4 Ah/h
Fuel Cell	12.5 kW P&W

orlando8

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Fullerenes for Hydrogen Storage

Fullerene-Based Porous Carbon Electrodes

and

Conducting Fullerene-Based Nanotube Materials

(CFNM)
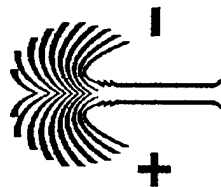
J.W. Van Zee

Center for Electrochemical Engineering

Department of Chemical Engineering

University of South Carolina

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Department of Chemical Engineering
University of South Carolina
Columbia, SC 29208

324
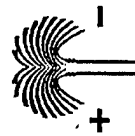
Collaborators

- J.M. Tour, Department of Chemistry & Biochemistry
  University of South Carolina

- Y.P. Sun, Department of Chemistry
  Clemson University

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Literature Reports

- $C_{60}H_2$

  J. Electrochem. Soc..,

- Heben et al. in Fullerenes

- Smalley et al. ~70% single walled nanotubes

  - Science

-

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Objectives

- Synthesize Conducting Fullerene-Based Nanotube Materials (CFNM)

  - Soot, Nanotubes, Fullerenes, Porous Carbon
  - Metal-like Conductivity
  - Hydrogen Storage Capacity > 5% by wt.

- Characterize Electrochemical Behavior of Material

- Fabricate Electrodes & Hydrogen Storage Material

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Objective: Synthesize CFNM Materials

- ## Systematic Synthesis Program-Doping

  - ### Rare earth & transition metal elements

  - ### Intermetallic Compounds -AB_5

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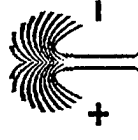
Objective: Characterize

- Chemical Yields - Function of Metal

  - Independent Variables:

    - Current, Gap Voltage, He Flowrate, Pressure
    - Temperatures of Feed Gas & Bath Water

  - Dependent Variables:

    - Graphite consumption, Total Mass Deposited
    - Soot, Nanotube and Fullerene Yield

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Schematic 1. Synthesis Reactor

VACUUM PUMP

WATER OUT

MERCURY MANOMETER

25 mm rubber tubing

rubber septum

Pyrex® guide arm

SUBMERSIBLE PUMP

VOLTMETER

flow control valves

oil manometer

copper mounting rod

arc

HELIUM CYLINDER

FLOW METER

WATER IN

graphite electrode

1 L Pyrex® reactor vessel

SHUNT

VOLTMETER

AC METER

DC ARC WELDER

220V/50 A AC OUTLET

SCALE: ⊢ = 1 cm

330

Objective: Characterize

- Dependent Variables Physical Properties

  - BET surface area, conductivity, thermal degradation profile, heat capacity

  - Qualitative: TEM & SEM photographs
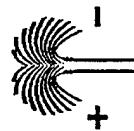
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Objective: Characterize

- Electrochemical Behavior

  - cyclic voltammetry

  - galvanostatic charge/discharge

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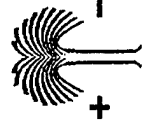
Electrochemical Behavior

- Charging the CFNM

- $H_2O + e-$ $\longrightarrow$ $H_{ads} + OH-$ $\qquad U = -0.83\ V$

- $H_{ads} + H_{ads}$ $\longrightarrow$ H_2

- $F + H_{ads}$ $\longrightarrow$ $F\,H$

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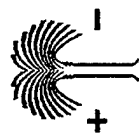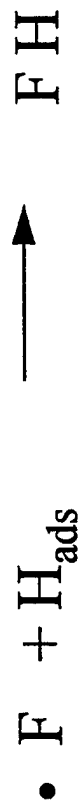
Separation of Soot

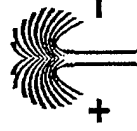- Arc-generated = Soot, Nanotubes, & Fullerenes

- TGA Results: 3% loss from 90-500C

  - 7% loss from 500-800C

- Oxidize in Air = soot gone but low yields

- Use CoS and NiS to increase nanotube yield
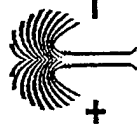
- Chemical Separations & Nanotube functionalization

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Chemical Hydrogenation of Fullerenes

- Birch reaction on CFNN material

  - Results: Carbon/Hydrogen Ratio = 3/1   3% of total carbon

- Birch reaction on Fullerene - Literature

  - Results: $C_{60}H_{36}$ = 4 %

- Birch Reduction on Polyfullerenes

  - Results 3-4%

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Table 1. Starting Metal Complex, Composite Electrode Properties, and Soot Properties.

Metal Complex	Trace Elemental Composition of Remaining Ligand in Graphite/Metal(0) Electrodes[a]	Metal(0) Particle Size in Graphite/Metal(0) Electrodes by XRD (nm)[c]	Metal(0) Particle Size in Graphite/Metal(0) Electrodes by TEM. average, range (nm)[e]	Single-Walled Nanotubes Observed in Soot? (size in nm)[g]
$Co_2(CO)_8$	---b	13	7.9, 1.4-24.1	yes (1.0-1.4)
$Ag(NO)_3$	N = 338 ppm	41	7.6, 1.8-24.4	no
$Fe(NO_3)_3 \cdot 9H_2O$	N = 415 ppm	36	11.6, 1.7-31.0	yes (1.0-1.4)
$CoCl_2 \cdot 6H_2O$	Cl = 88 ppm	---d	8.9, 1.1-58.3	yes (1.0-1.4)
$CuCl_2 \cdot 2H_2O$	Cl = 1.36 %	39	8.8, 1.7-37.7	no
$LaCl_3 \cdot 7H_2O$	Cl = 2.74 %	---d	---f	no
$NiCl_2 \cdot 6H_2O$	Cl = 456 ppm	33	6.2, 1.9-23.3	yes (1.4-1.6)
$PtCl_4$	Cl = 0.46 %	36	11.1, 2.2-35.0	yes (1.6-1.8)

Effect of Charge Time on H_2 Capacity

Legend:
- Run Date: 7/23/96 Charge Time: 60 min
- Run Date: 7/31/96 Charge Time: 120 min
- Run Date: 7/31/96 Charge Time: 90 min
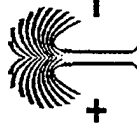- Run Date: 8/1/96 Charge Time:180 min

X-axis: Time (min)

Y-axis: Potential vs SCE (V)

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10 mA/cm² Charge Curves
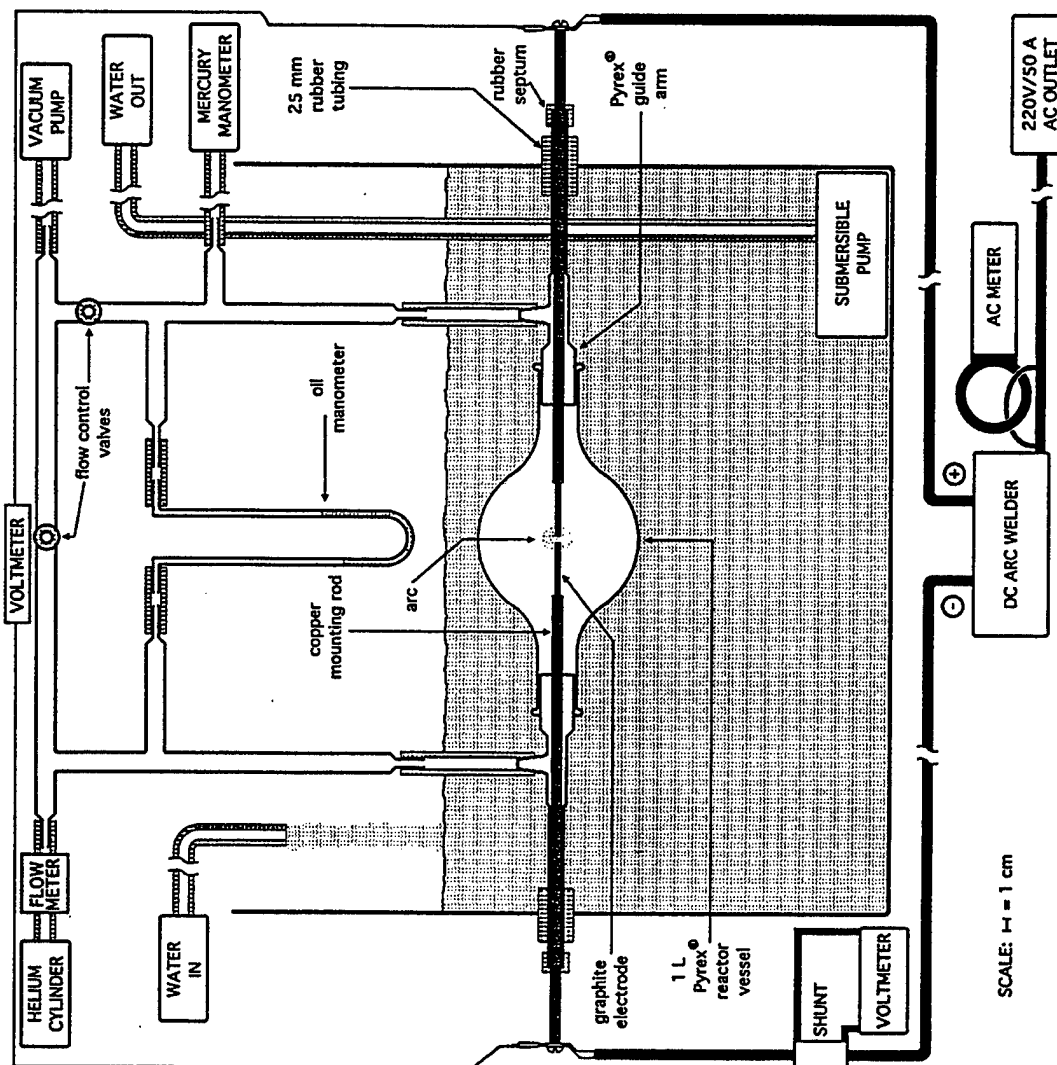
338

10 mA/cm² Discharge Curves

Potential vs SCE (V)

Time (min)

C$_{60}$/Teflon

MER C Binder

MER Ag Binder

Activated Carbon/Teflon

J.W. Van Zee, "Fullerene-Based Materials" for the
Workshop on H$_2$ Storage and Generation Technologies for
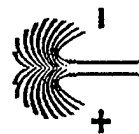Medium -Power and Energy Applications, April 9, 1997

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10 mA/cm² Charge Curves

Co Nanotubes

Ni Nanotubes

Activated Carbon/Teflon

C₆₀/Teflon

Time (min)

Potential vs SCE (V)
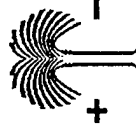
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10 mA/cm² Discharge Curves

C₆₀/Teflon

Co Nanotubes

Ni Nanotubes

Activated Carbon/Teflon

Potential vs SCE (V)

Time (min)

341
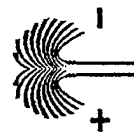
Summary of H2 Storage Capacity

Material	mAh/g	mAh/l	wt %	g/cm$_3$	Wh/Kg	Wh/l
Present CNM	54	49	0.2	1.1	54	49
Birched CNM	804	731	3.0	1.1	804	731
Future CNM	2,140	1,950	8.0	1.1	2,140	1,950

GRAPHITE NANOFIBERS: A CATALYTICALLY ENGINEERED MATERIAL

M. S. Kim, C. Park, A. Chambers, R. T. K. Baker and Nelly M. Rodriguez
Department of Chemistry, Northeastern University, Boston, MA 02115, USA

ABSTRACT

Graphite nanofibers are a newly developed material produced from the decomposition of selected carbon containing gases over certain metallic surfaces at temperatures ranging from 400-800°C. The solid consists of graphite platelets perfectly arranged in various orientations with respect to the fiber axis, where the degree of crystalline perfection of the deposited fiber is dictated by the chemical nature of the catalyst particle, the composition of the reactant gas and the temperature. One of the most outstanding features is the presence of large number of edges, which in turn constitute sites readily available for chemical or physical interaction. From the physical point of view, graphite nanofibers vary from 5 to 100 μm in length and are between 5 to 50 nm in diameter. From *in-situ* electron microscopy studies it has been possible to determine the key steps leading to the formation of graphite nanofibers. When a hydrocarbon is adsorbed on a metal surface and conditions exist which favor the scission of a carbon-carbon bond in the molecules then the resulting atomic species may dissolve in the particle, diffuse to another set of faces and ultimately precipitate at the interface to form a graphite nano-structure. Surface science studies have revealed that dissociative chemisorption of the hydrocarbon only occurs in particular faces possessing certain crystallographic orientation and that the reaction can be enhanced by certain adatoms or by the presence of coadsorbed molecules such as CO. It is believed that a combination of electronic and geometric effects are operative that not only promote the dissociation of the hydrocarbon, but also alter the mode of adsorption of the hydrocarbon on the metal surface. Preliminary data obtained in our laboratory has demonstrated that when these structures are exposed to hydrogen at moderate pressures, they are capable of absorbing and retaining large quantities of the gas at room temperature. It is clear from this data that graphite nanofibers are an exciting new type of material that has tremendous potential as a hydrogen storage medium.

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Graphite Nanofibers: A Catalytically Engineered Material

M. S. Kim, C. Park, A. Chambers,
N. M. Rodriguez and R. T. K. Baker

Factors Involved in Nanofiber Growth
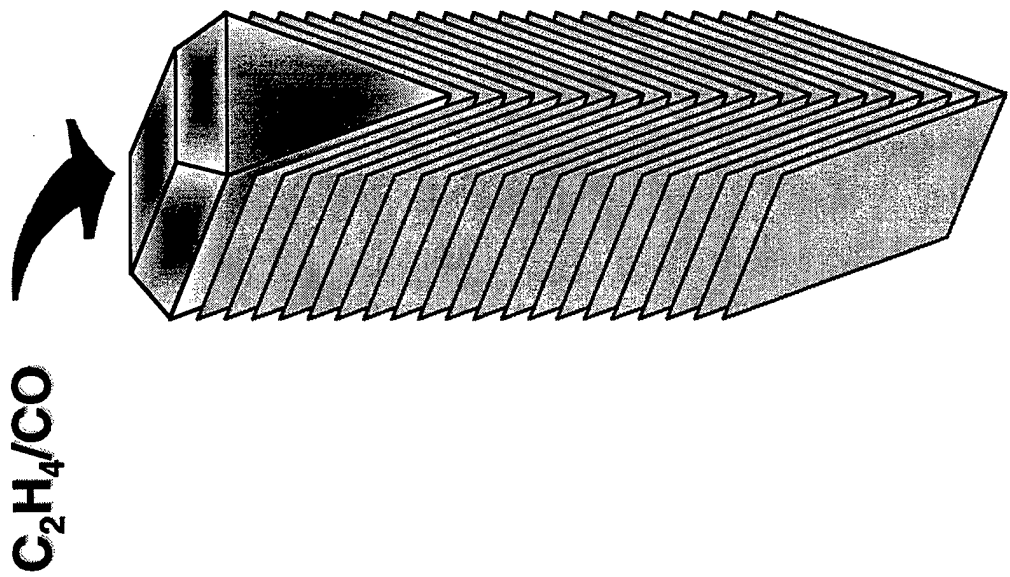
C_2H_4/CO

Metal-Gas Interface

Diffusion of Carbon through Metal

Precipitation of Graphite Platelets at the Metal-Carbon Interface

Metal-Gas Interface

C₂H₄ over Modified Metal Surfaces

Adatom

C₂H₄
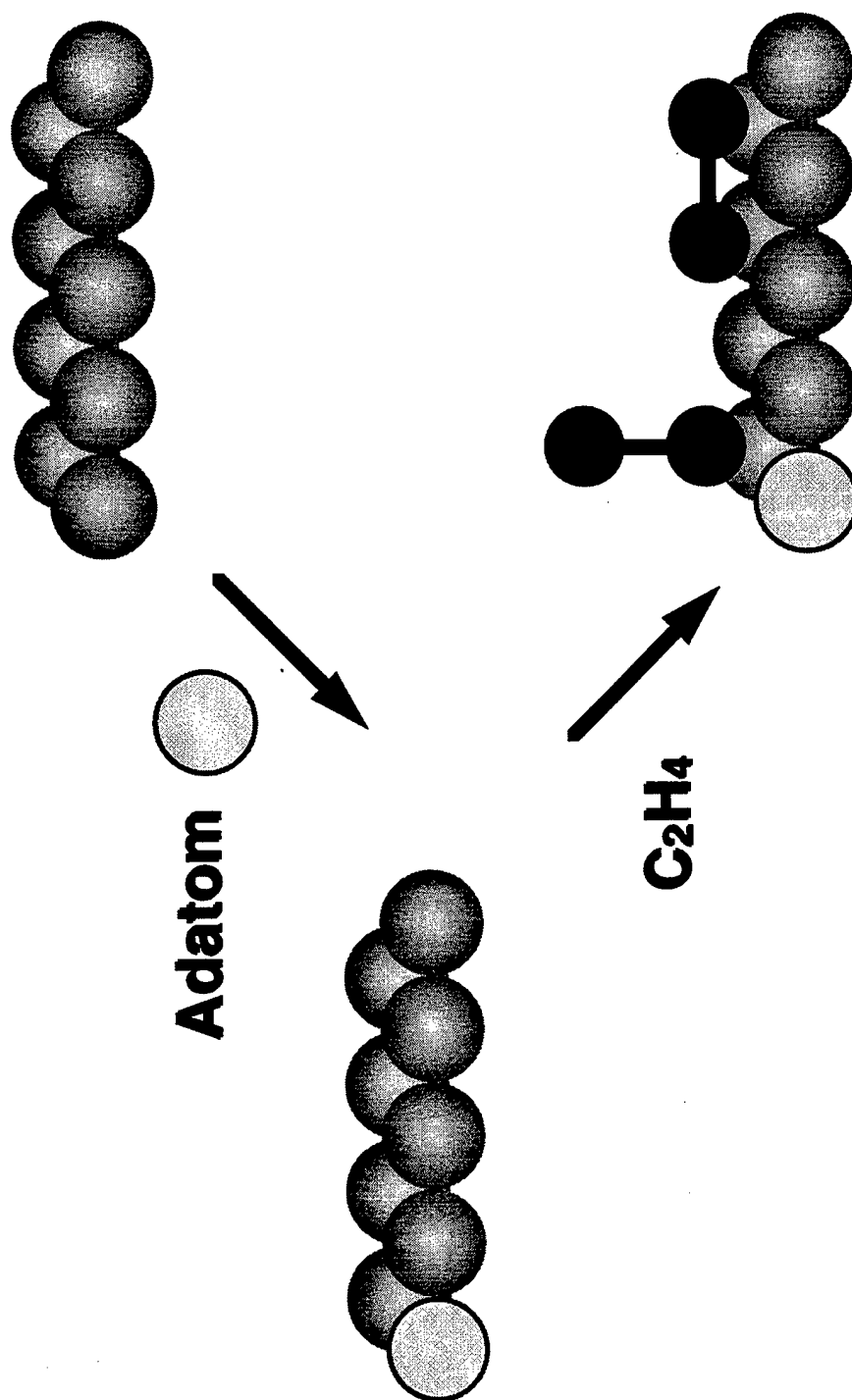
Ethylene over Metal Surfaces

CO or H₂

C₂H₄

C₂H₄/H₂

348
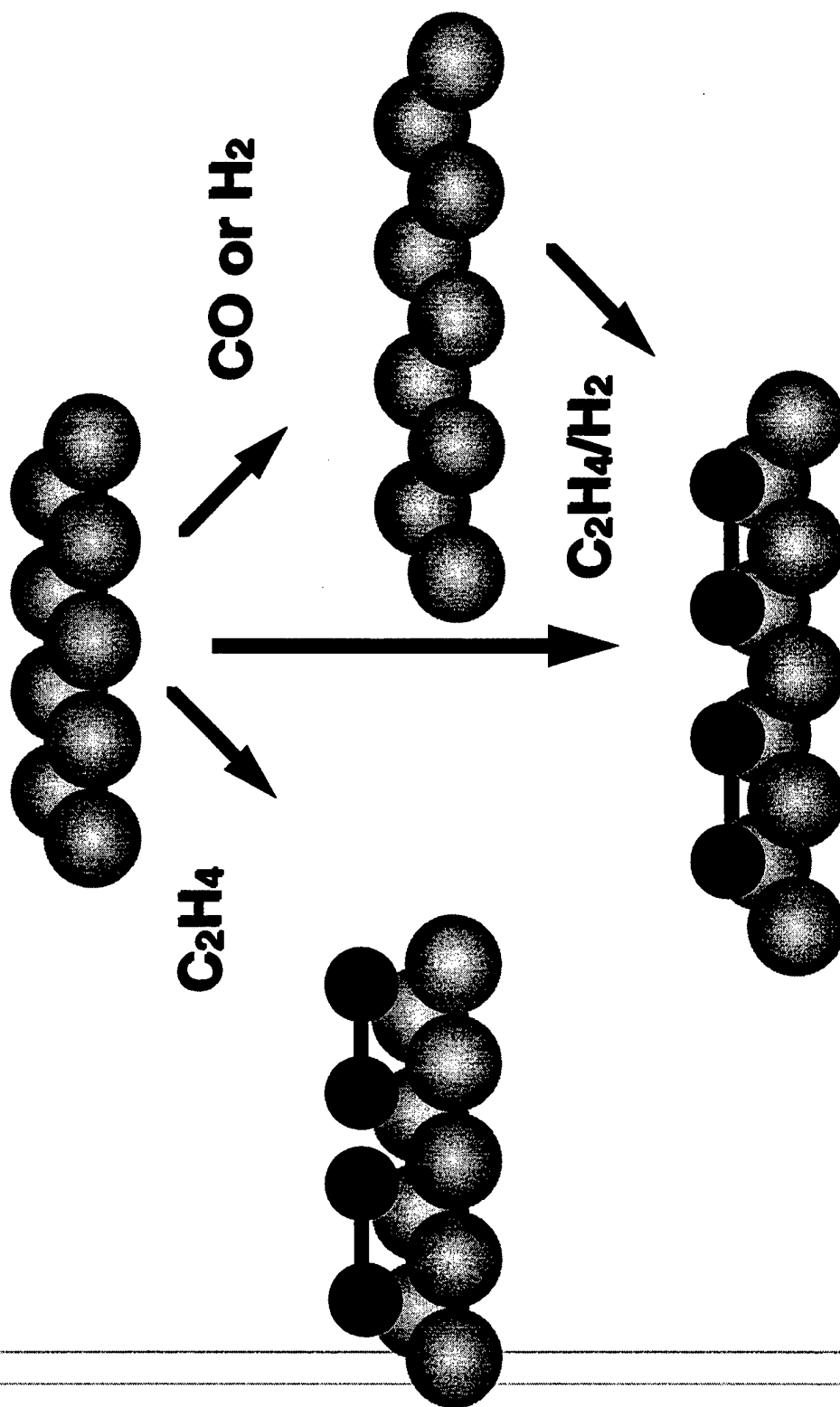
Gas/Metal Particle Interactions

- Surface science studies have established that the interaction of a given gas molecule with a metal surface is frequently limited to certain crystal faces.

- This phenomenon is governed by geometric arrangements of the metal atoms in concert with the bond distance of the gaseous molecules, as well as the establishment of electronic interactions.

- When a gas is chemisorbed on a metal surface, a concomitant weakening of the intermetallic bond strength occurs, and this induces mobility in the surface atoms of the solid – surface reconstruction.

Hydrocarbon/Metal Interactions

- When metal particles are undergoing reaction, distinct crystallographic faces are generated, some of which are capable of **dissociative chemisorption** of the hydrocarbon, but are unable to **precipitate dissolved carbon atoms**, and another set of faces that exhibit the reverse properties.

- A corollary of this phenomenon is that certain metal faces remain free of solid carbon and available for continued reaction with the hydrocarbon.

- The presence of the carbon deposit structure effectively **preserves the shape of the metal particle** in the reactive state during subsequent cooling.

Metal-Carbon Interface

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Graphite Precipitation on Ni(111)

Ni

C
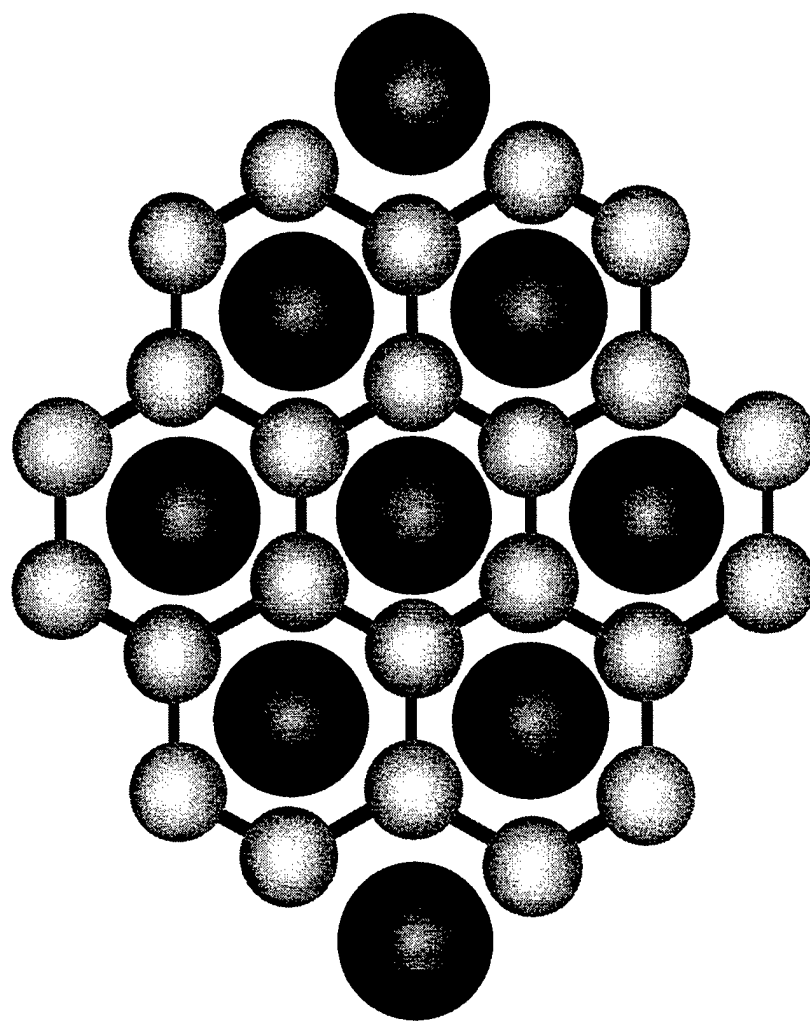
Yang and Chen, J. Catal. 115, 52 (1989)

Carbon Nanofiber Structure

C$_2$H$_4$ /CO
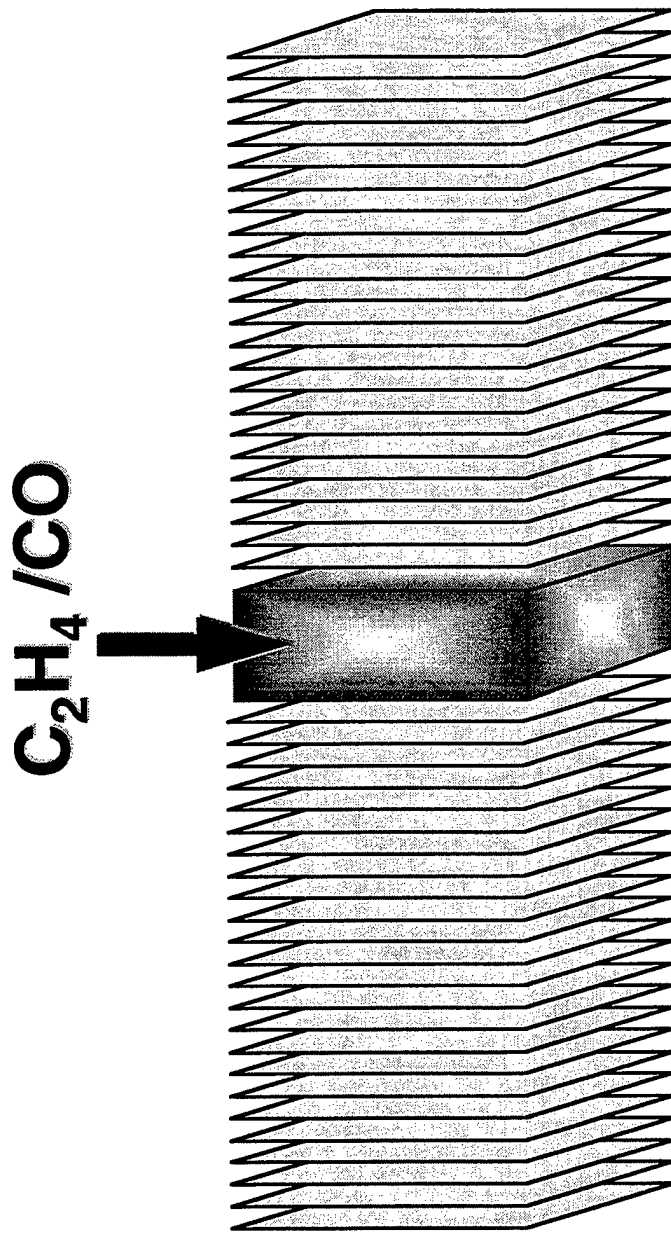
- Four faces where hydrocarbon decomposition occurs.
- Two faces where carbon precipitation takes place.

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Carbon Nanofiber Structure

C_2H_4

- Two faces where hydrocarbon decomposition occurs.
- Four faces where carbon precipitation takes place.

Carbon Nanofiber Structure

C_2H_4
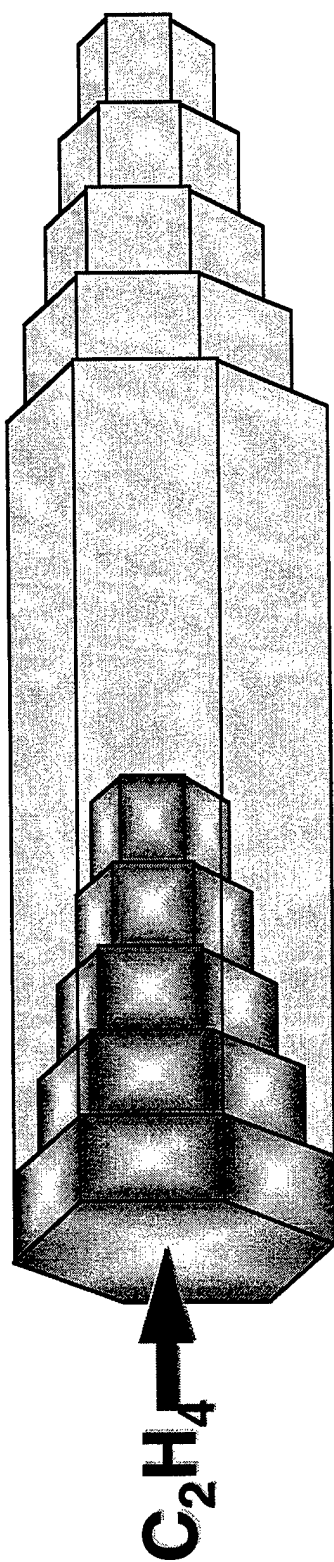
- One face where hydrocarbon decomposition occurs.
- Several faces where carbon precipitation takes place.

Variations in Particle Morphology
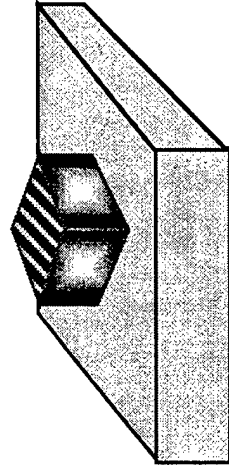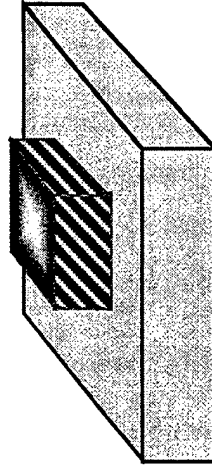
Rhombohedral   Cubic   Hexagonal
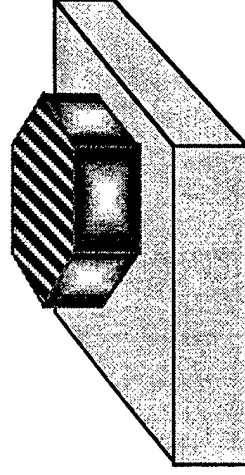
- Particle shapes are influenced by temperature, nature of afsorbate gas and support structure.

- Cross hatching denoted faces where hydrocarbon dissociation occurs.

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Graphite Nanofibers in Hydrogen Storage

Ideal Hydrogen Storage Medium

- The failure to produce a practical gas storage system has prevented hydrogen from reaching the commercial forefront as a transportation fuel.

- The ideal system should be:
  - ◆ lightweight,
  - ◆ compact,
  - ◆ usable at moderate temperatures,
  - ◆ relatively inexpensive,
  - ◆ reusable without the need for regeneration,
  - ◆ safe.

- Graphitic nanofibers appear to fulfill most of these criteria.

Hydrogen Storage Systems

Storage System	Advantages	Disadvantages
Compressed gas	economical	hazardous, bulky
Metal hydrides	compact, safe	expensive, heavy
Liquid hydrogen	high density	cooling/ insulation
Cryo-adsorption on various solids	moderate size/ moderate cost	cooling/ insulation
Non-cryogenic: Graphite Nanofibers	compact, light economical	supply

Adapted from J. S. Noh, R.K. Agarwal, and J. A. Schwarz, Int. J. Hydrogen Energy 12, 693 (1987)

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Hydrogen Diffusion in Graphite

$\{1\bar{1}21\}$

$\{10\bar{1}1\}$
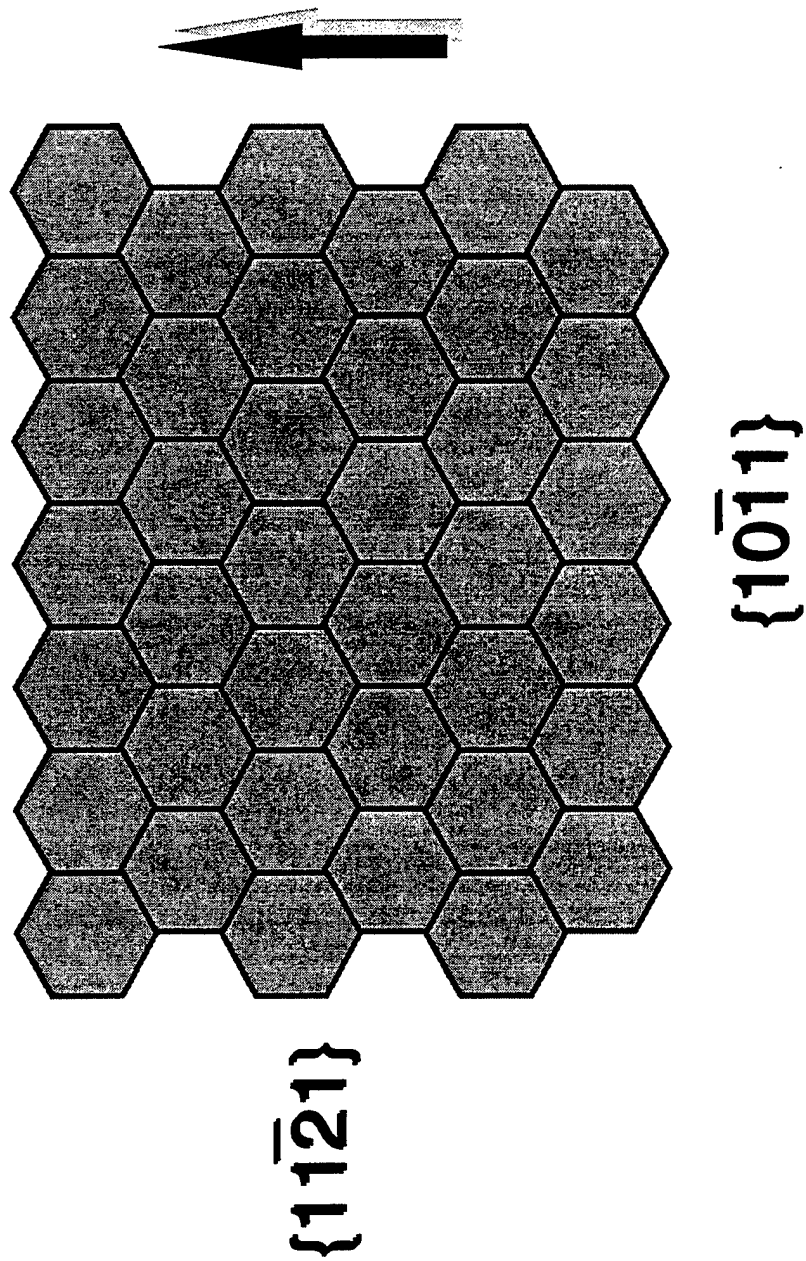
Adsorption/Desorption of H$_2$

- The adsorption process appears to be controlled by diffusion of H$_2$ between the graphite layers.

- It is evident that the capacity far exceeds that of a monolayer storage. These high values suggest that the phenomenon occurs via a capillary condensation process, and that once H$_2$ is trapped inside the structure, the molecular size of the gas reverts to that of the covalent state.

- The π-electrons of the graphite basal plane are believed to play a key role in enhancing the sticking coefficient of H$_2$ within the structure.

Adsorption/Desorption of H_2

- Upon reduction of the pressure to atmospheric conditions, a large fraction of the stored H_2 is released.

- There is, however, ~15% that is strongly held within the nanofiber structure and is only released upon heating to temperatures in excess of 500°C.

- During the adsorption step, it is possible that the nanofiber structure undergoes swelling and upon release of the H_2, the initial structure is regenerated.

- Examination of the nanofibers that have been subjected to up to two cycles by HRTEM, indicates that the structures have maintained their integrity.

4. SUMMARY OF WORKING GROUP DISCUSSIONS

4. Summary of Working Group Discussions

The attendees were assigned to three working groups: Physical/Absorptive Systems, Chemical Hydrides and Related Materials, and Thermal and Catalyzed Processes. The Working Groups were each assigned a Chair and a Scribe. The working groups were charged with discussing the technologies assigned to the group and hearing additional technical presentations from attendees. After discussions and presentations, the Working Groups were further charged to complete several tables summarizing the material characteristics, required ancillaries, time to implementation, significant issues and barriers, and the three mission-specific estimates of system weight and volume for each technology. Finally, the Chair and Scribe for each group were asked to prepare the summary tables and a short written discussion of the Working Group findings. What follows here in Section 4 is an overview of the working group findings prepared by the authors of this report. Section 5 contains the written report and summary tables prepared by the Chair and Scribe of each of the three Working Groups. Also included in Section 5 are copies of additional visual materials presented by participants in the working groups.

The Working Group on Physical and Absorptive Storage considered nine technologies, grouped into four categories as follows:

Ambient temperature, pressurized hydrogen gas storage
- Lightweight, high-strength cylinders
- Engineered glass microspheres

Reversible metal hydrides
- Low-temperature dehydrogenation (ambient to ~ 100 °C)
- High-temperature dehydrogenation (> ~ 250 °C)

Carbon-based absorbents
- Fullerenes
- Carbon nanotubes
- Carbon nanofibers

Irreversible chemical hydrides
- Hydrolyzable chemical hydrides
- Thermally-decomposable chemical hydrides

Pressurized tank technology uses light-weight carbon-graphite composite fiber wrapped tanks, with a metallized plastic liner. These tanks have been pressurized to 15,000 psi. Tank technology has been demonstrated in the commercial sector (for fuel-cell powered municipal buses, for example) as well as for the DoD, and could be implemented in a short time (1-3 years). Among the strengths of this technology are: pressurized tanks are very efficient on a mass basis (hydrogen densities exceeding 0.10 kg H_2 per kg of system weight); the load following and response time characteristics are good and delivery is thermoneutral.

Improvements in the pressurized tank technology can be achieved with the development of small, fully-metallized plastic liners and lighter-weight regulators and valves. The necessary valves and restrictors are the heaviest components for such systems, and pressurized tanks are very efficient on a mass basis (hydrogen densities exceeding 0.10 kg H_2 per kg of system weight), however, the volumetric efficiency is not as high as metal hydrides and some other ma-

terials due to the low density of compressed hydrogen. The bulkiness and large profile associated with a hydrogen tank could present major difficulties for a man-portable system. The time to refill a hydrogen tank in the field and the necessary transportation infrastructure for field applications are also weaknesses. The overwhelming concern associated with this technology is safety. The potential for explosion should a hydrogen vessel be pierced is significant in combat situations. With a technology this close to commercial application, the DoD may wish to consider a comprehensive safety review of pressurized tank technology in the context of battlefield needs. This could identify applications in which the technology is appropriate and those in which it is inherently unacceptable.

Delivery of gaseous hydrogen is essentially thermoneutral, unlike the dehydrogenation of reversible metal hydrides which may require significant heat input, or the irreversible reactions of chemical hydrides which release significant heat. However, rapid refilling of hydrogen tanks does require cooling because the hydrogen temperature increases markedly during refilling. The potential for explosions should a hydrogen vessel be pierced is serious under combat situations. Workshop participants viewed a photograph of a composite wound container which had taken a live round without exploding, but it was also stated that firing a tracer round into the container resulted in detonation.

Engineered glass microspheres are hollow pressure vessels on the order of 50 microns which hold hydrogen under high pressure. The microspheres are filled by heating them in excess of 250 °C under a high-pressure hydrogen atmosphere. Safety considerations are much improved compared to a single pressurized tank. The 3M Corporation presently manufactures such microspheres in bulk. It is proposed that controlled delivery of hydrogen could be accomplished by embedding them on an adhesive tape, for instance, and feeding the tape to a mechanical crusher. This is a promising concept but no prototype hydrogen release system has been built. Also, there is at present no infrastructure for large-scale manufacturing and filling of the microspheres. This technology could be developed in a medium time frame (3-5 years) with research on scale-up and quality control in the manufacturing of the microspheres, and development of efficient means for the filling with and releasing of hydrogen.

The physics and chemistry of both low-temperature and high-temperature reversible metal hydrides are fairly well known and have been the subject of several decades of scientific research. Low-temperature metal hydrides have poor weight efficiencies (low hydrogen loading) but (depending on the alloy) will release hydrogen at 50-80 °C and at low pressures. High-temperature hydrides have much higher hydrogen storage capacities (6 weight percent, not including containers and ancillaries) but must be heated well in excess of 100 °C to release hydrogen. This implies that significant heat must be provided. For both low- and high-temperature hydrides, the kinetics of dehydriding are an important issue when it comes to starting, stopping, and controlling a fuel cell with varying load demand. The crucial research needs are to engineer a heat source and to control the kinetics of hydrogen liberation to meet demands.

Carbon fullerenes with 6 weight percent hydrogen loading have been experimentally achieved. Like reversible metal hydrides, significant heat input is required to liberate hydrogen gas. Another critical issue is manufacturing capability and cost: additional research and development will be needed to reduce the manufacturing cost; a near-term goal is to reduce the cost to approximately $25/kg. Fullerenes can be hydrogenated electrochemically or catalytically, but the choice of solvent, catalyst, pressure and temperature appear to greatly alter the hydrogen

loading and dehydrogenation kinetics. These materials are much less understood than metal hydrides and therefore the time to possible implementation is longer, at least 3-5 years.

Single wall nanotubes are related to the fullerenes and are graphite sheets joined to form long cylinders. Experiments have shown 5-10 weight percent hydrogen storage capacity. The mechanism of hydrogen storage is thought to be the entrapment of absorbed hydrogen within the nanotubes. The notable issues of cost, manufacturability, hydrogen loading and release, are essentially the same as for carbon fullerenes.

Graphite nanofibers are individual graphitic bundles grown by decomposition of ethylene/CO (or other hydrocarbon/CO mixtures) on metal catalyst particles. One research group at Northeastern University has reported hydrogen storage on these materials. It is claimed that up to 50 weight percent hydrogen can be absorbed by the fibers when they are exposed to several hundred atmospheres of hydrogen for 24 hours, and that 80% recovery of this hydrogen is attained at room temperature by decreasing the pressure to ambient conditions. These claims are revolutionary, but verification is needed. Should these claims be substantiated, additional research and development is needed on synthesis and scale-up to commercial production capacity.

The Working Group on Chemical Hydrides and Related Materials considered four broad categories of materials. Within each category, several similar materials can be identified which store and release hydrogen by similar mechanisms. The four categories considered were:

- Hydrolysis of organosilanes and organoboranes

- Solid-state decomposition of chemical hydrides

- Reversible hydrogenation and dehydrogenation of cycloalkanes

- Hydrolysis of classical chemical hydrides

Organosilane chemistry is being developed by SRI, and allows generation of hydrogen by catalytic reaction with water in a homogeneous liquid phase. Ethenyl silane, ethynyl silane, and phenyl silane presently appear to be good candidates for hydrogen storage. Depending on the particular organosilane used, the theoretical mass yield of hydrogen ranges from 6.2 to 9.8 weight percent, assuming 100% conversion of the reaction and no excess of reactant. The heat of reaction appears to be low. The systems proposed are liquid-phase which may greatly simplify the metering and control of hydrogen production. The time to potential implementation is at least 3-5 years, and requires additional research and development on fundamental kinetics, actual hydrogen yields, thermochemistry, stability, safety, toxicity, by-product disposal, and system design. No production infrastructure exists for large-scale manufacturing of these compounds, and therefore the cost of materials is still a significant unknown.

Solid state decomposition of classical chemical hydrides (*e.g.,* $LiBH_4$, $LiAlH_4$) is a chemistry that is well-known. It is possible to accomplish the reaction in essentially 100% yield and with little excess reactant, leading to storage capacities of approximately 8-10 weight percent. The reaction mixture combines the chemical hydride with ammonium chloride or similar halide salt, and the mixture is stabilized with a polymer binder. This renders the reaction mixture stable for storage and transport, unlike the neat chemical hydrides which are sensitive to air and moisture. The reaction must be initiated with a high temperature ignitor such as a squib fuse or pyrotechnic. Once initiated, the reaction cannot be stopped and is highly exothermic.

The production scenario is to package the solid reaction mixture in a number of discrete packets and selectively ignite the reactants as hydrogen is needed. Hydrogen is produced rapidly and a surge tank or equivalent arrangement is required for load-leveling. This would raise some of the same safety concerns as were discussed under "pressurized gas storage." Commercial units for production of hydrogen from this mechanism are now available from Royal Systems, and it is believed that modifications will allow them to be used for unattended operation of low-power remote sensing stations. The thermal signature and safety of such devices for man-portable applications are significant issues. The reactions are irreversible so the reaction products would have to be disposed or recycled. The main avenue for further development would appear to be incremental improvements on existing system designs, and careful comparison of the properties of the various chemical hydride candidates to select the optimum chemistry.

Cyclic organic compounds such as decalin and methylcyclohexane are liquids which can store and release hydrogen by the reversible hydrogenation and dehydrogenation of the ring structure. This process takes place at elevated temperatures in the presence of a catalyst. MER Corporation is evaluating well-known heterogeneous hydrogenation/dehydrogenation catalysts based on supported nickel, palladium, or platinum, with platinum being the most effective. The University of Hawaii is evaluating a novel class of homogeneous catalysts which incorporate P-C-P "pincer" ligands around iridium. This reaction is thermodynamically limited and must take place at elevated temperatures ($> 200\ ^{\circ}C$), although catalytic activity was reported at temperatures as low as $100\ ^{\circ}C$. Thermal signature and the energy required to produce and maintain these temperatures is a major concern, as are the kinetics and control of the reaction. Theoretical hydrogen yields are slightly in excess of 7 weight percent, and the raw materials (cyclic hydrocarbons) are readily available. The materials are inherently recyclable, although long-term degradation after many uses has to be determined. Among the major issues would be development of miniature "chemical plants" to accomplish the production of hydrogen at the small scales of interest in this workshop.

Classical chemical hydrides such as CaH_2, LiH, $LiBH_4$, $LiAlH_4$, $NaBH_4$, and $NaAlH_4$ produce hydrogen upon contact with liquid water. The reaction is strongly exothermic and is favored thermodynamically, but in many cases the kinetics are inhibited by the high pH and the insolubility of the reaction products. The reaction is irreversible, so the by-products must be recovered and either recycled or disposed. Some variation on the well-known Kipp generator is used to contact the water and the hydride. Commercial units are available from A.F. Sammer, and the Snorkeler fuel cell system also has a hydrolysis unit available as one hydrogen source. The $NaAlH_4$ chemistry described by RTI in Working Group 1 is of the same general concept as was considered by Working Group 2.

The weight and volume efficiencies of these materials appear competitive with other known technologies in that 7-8 weight percent hydrogen can be produced from a stoichiometric reaction. However, in practice excess water is almost always required. Attitude sensitivity is an issue with these systems, as is safety. Most of the hydrides are moderately to very unstable when stored in humid air. The strong exothermic nature of the reaction and the instability of some materials has led researchers at the University of South Carolina to use organic ligands to stabilize the compounds, at the cost of additional molecular weight. Research at the U.S. Air Force Academy concerns a proprietary chemical hydride with a theoretical hydrogen yield exceeding that of $LiAlH_4$. Because commercial units are available this approach to hydrogen storage and delivery could be considered more mature than others, but field implementation still re-

quires solutions to the problems of safety, attitude sensitivity, and metering and control of the reactants. Appended to these Workshop proceedings is a review of work conducted at Texas A&M University where these considerations are discussed in more detail. At present, improvements in this approach will most likely be due to incremental improvements in engineering design and packaging, and to identifying the optimum chemical hydride compounds.

The Working Group on Catalyzed and Thermal Processes examined seven different liquid or gaseous fuels which would be reprocessed to produce hydrogen gas. These fuels were ammonia, methanol, propane, methane, butane, gasoline, and diesel fuel. All fuels except ammonia would produce carbon monoxide which will poison present PEM fuel cell catalysts, so elimination or reduction of CO is a significant issue in all systems except the ammonia reformer. Residual ammonia must also be eliminated from any stream fed to the fuel cell.

Ammonia reforming by thermal decomposition was the subject of an invited presentation by Analytic Power. The thermal decomposition products are hydrogen and nitrogen, but the decomposition must take place at very high temperatures in order to reduce the ammonia residual to ppm levels or less. Unreacted ammonia in the effluent will poison the PEM catalyst, so a combination of high conversion efficiency and an ammonia scrubber for the reactor effluent are necessary. Ammonia has a very high theoretical H_2 yield. It can be stored as a liquid under modest pressure and is very inexpensive due extensive use in large-scale industries. Unlike all the other liquid fuels discussed in this working group, ammonia reforming produces no carbon monoxide which is another PEM catalyst poison. Analytic Power has contracted to deliver a small-scale thermal ammonia reformer within one year of the date of this workshop.

Methanol, ethanol, gasoline, and other hydrocarbon fuels can be converted to hydrogen and by-products either by partial oxidation (POX), or by a combination of partial oxidation and steam reforming (PROX). In this working group, both routes were discussed under the heading "Mesoscopic Fuel Processing," a term employed by researchers at Pacific Northwest Laboratories to describe unit operations (heat exchangers, reactors, fuel cells) which have been miniaturized to a scale of cm in dimension. Arthur D. Little has developed a fuel processor which will convert natural gas, propane, gasoline, methanol, ethanol or diesel fuel to hydrogen. Further reduction of the product gas with steam produces 50 ppm CO in the outlet gas. The ADL system is not portable because the unit operations have not been miniaturized.

Large-scale hydrocarbon reforming plant technology is well-known, so a significant issue in this area is the miniaturization of process units to meet the mission requirements of the DoD. It was the consensus of the working group that the mesoscopic fuel processors described by PNL are at least 2-3 years away from laboratory demonstration. The working group felt that power plants of 100 W and above were likely to be developed, but that the likelihood decreased as the power requirements grew smaller because of the uncertainty of scaling down process equipment and the ancillary equipment required.

5. RESULTS AND RECOMMENDATIONS OF WORKING GROUPS

WORKING GROUP 1: Physical/Absorptive Systems

Physical/Absorption Working Group

The participants in Session 1 were:

Mark Debe, Chair	3M Company
Mike Heben, Scribe	National Renewable Energy Lab
Thomas George	Sandia National Laboratory
Brian James	Directed Technologies
Michael Monsler	W.J. Schaeffer Associates
Jim Ohi	National Renewable Energy Lab
Jim Reilly	Brookhaven National Laboratory
Nelly Rodriguez	Northeastern University
Jim Stephens	CECOM, U.S. Army
John Van Zee	University of South Carolina
Ricardo Schwarz	Los Alamos National Laboratory
Alan Bartolome	U.S. Army, Ft. Meade, MD
Henry DeRonck	International Fuel Cells
Jack Evert	3M Company
Michael Heben	National Renewable Energy Lab
Art Kaufman	H-Power
Myung Lee	Savannah River Site
Fred Mitlitsky	Lawrence Livermore Natl. Lab.
S.R. Narayanan	Jet Propulsion Lab, Battery Group
Krishna Sapru	Ovonics/Energy Conversion Devices
Kenneth Stroh	Los Alamos National Laboratory
John Cleland	Research Triangle Institute
Valentin Serebrennikov	MAGNIC International, Inc.
Xiao Lu	MER Corporation

The Physical/Absorption Working Group considered ten technologies belonging to four classes of materials for hydrogen storage. These include pressurized tanks, pressurized glass microspheres, four types of metal hydrides, and three types of carbon based materials. Material characteristics and mission-specific weight and volume estimates are summarized in Tables 1 and 2, found in the Executive Summary. Tables 4 and 5 outline evaluations of the individual technologies and issues associated with each system and are presented at the end of this section.

Pressurized Tank

The pressurized tank technology has been developed to an advanced degree and was considered to have the highest proven H_2 yield potential, approaching 0.18 kg H_2 per kg of containment and peripherals (Table 1). This is based on carbon-graphite composite fiber-plus-resin overwrapped tanks with lightweight plastic liners, and a safety factor (burst pressure/ operating pressure) of 1.5 for tanks pressurized at 15,000 psi. Fabrication issues for this technology include demonstration of fully metallized polymer bladder liners, determination of the appropriate safety

design factor (1.5 versus 2.25), availability of lightweight pressure reducers and solenoid valves for high pressure operation, and cost (Table 4). Implementation issues include safety (burst and shrapnel hazards), fast filling heating rise (40% increase in tank temperature), thermal cycling and the need to have a central (mobile) station available for refilling (Table 5).

Glass Microspheres

The glass microsphere technology is also storage by pressurized containment, however the containers are hollow glass bubbles (microspheres) with diameters on the order of 50 micrometers (0.002 inches) with wall thicknesses of about 1 micrometer. It is believed possible to pressurize bubbles up to 9000 psi with sufficiently high glass strength and sufficiently low aspect ratio (diameter/wall thickness). With packing factors around 0.55, the internal volume of the bubbles available for hydrogen storage is approximately 0.47 of the outer container, giving hydrogen storage per unit volume equivalent to a pressurized tank approaching 4200 psi. However the outer containment does not have to be able to withstand much more than ambient pressure. This is considered to offer a significant safety advantage. The theoretical hydrogen yield of containerless or unsupported bubbles holding 9000 psi at 300 K would be 0.087 kgH$_2$/kg of bubbles, or 8.7 wt% (Table 1).

One possible means for delivery and release of the hydrogen was described in which the bubbles are coated on a thin tape support and rolled into a cartridge. The hydrogen is released by fracturing the bubbles, e.g. by passing the tape through a pair of crushing rollers, at the rate required by the fuel cell and its load, using feedback control of a drive motor. When the tape is expended, it can be replaced easily by a new cartridge. The hydrogen release can be quickly stopped and started as often as necessary, and operated at ambient temperatures and pressures.

The primary issue centered on demonstrating the potential for large-scale manufacturing processes for both filling the bubbles and for fabricating bubbles of sufficient quality to withstand maximal hydrogen pressures of >6000 psi (Table 4). Filling involves heating the bubbles in high-pressure hydrogen. The permeability of hydrogen through the glass walls is a strong function of temperature and increases dramatically above about 250°C. Cooling the bubbles while under pressure locks the hydrogen inside. At room temperature the shelf life of the hydrogen-filled microspheres is years, but could be an issue for storage in hot environments for long periods of time.

Metal Hydrides

Two subclasses of hydrides were considered; reversible (low- and high-temperature metal hydrides) and irreversible (chemical and thermal hydrides). With the low- and high-temperature metal hydrides, increasing the hydrogen pressure or lowering the alloy temperature will cause the latter to absorb hydrogen. Decreasing the hydrogen pressure or raising the alloy temperature will cause hydrogen to be released. Plots of dissociation pressure versus reciprocal temperature conveniently fall into two groups for most metal hydride alloys, viz. high and low temperature. The high-temperature alloys are characterized by lower atomic weights and stronger (ionic) metal-hydrogen bonds, and therefore have the highest weight percent hydrogen. The low-temperature alloys have lower hydrogen yields, being characterized by covalent bonds and higher atomic weights.

Low-Temperature Metal Hydrides (reversible)- Low-temperature metal hydrides have been extensively studied for hydrogen storage. LaNi$_5$ is an intermetallic hydride considered most useful for hydrogen storage for PEM fuel cells, operating in the 50-80°C range. Hydrogen is stored

when the alpha phase ($LaNi_5$) converts to the beta phase, $LaNi_5H_6$, reaching a containerless theoretical hydrogen yield of 1.75 wt % (Table 1). All such reactions are exothermic, causing the compounds to heat up when loaded and cool when the hydrogen is extracted, so heat must be provided to release the hydrogen. A typical dissociation pressure at 50°C would be 4 atmospheres, requiring low pressure containment. No significant issues were identified other than the relatively low hydrogen storage capacity. The relatively low temperatures and pressures imply modest system integration issues (Table 5).

High-Temperature Metal Hydrides (reversible)- High-temperature metal hydrides offer considerably higher theoretical hydrogen storage yields (up to 6 wt%) than the low-temperature variety, but at the expense of additional ancillary heat sources and exchangers to facilitate dehydriding at temperatures in excess of 320°C (Table 1). A primary material example of this class which was considered is Mg - 23atom% Ni, with a theoretical yield of 5.4 wt% (no containment). A proposed means for supplying the dehydriding heat is a Thermite type heater, embedded in the metal hydride container. Typical dissociation pressures are close to 1 to 3 atmospheres so only modest pressure containment is required. The most significant issue identified was lack of stop/start flexibility because the high temperature generation device cannot be shut down after initiation. Research or resource needs identified were to develop advanced catalysts and heat sources.

The next two hydride cases discussed by Group 1 concern $NaAlH_4$ and AlH_3. These materials may have been more appropriately addressed Session 2, but were considered here with the metal hydrides. The source material is effectively consumed in the irreversible hydrogen release reaction.

$NaAlH_4$ + water (irreversible) - Hydrogen is spontaneously released when water contacts $NaAlH_4$. The proposed system discussed was a wafer or doughnut shaped solid pellet, with which contact with water could be controlled by a pressure release valve. The hydrogen is generated rapidly so the system has a rapid response time. The effect of the hydrogen pressure control valve is to limit the amount of water able to contact the surface of the pellet due to hydrostatic movement of the water column, which makes the device orientation dependent, unless designed with a bladder of some type. The theoretical hydrogen yield is 6 wt % without containment. The largest issues were believed to be system integration related, including supply of the water (Table 4).

AlH_3 (irreversible) – Igniting AlH_3 (dry) can potentially liberate 9 wt % hydrogen. The high hydrogen storage comes at the expense of control of the hydrogen release rate. Pressure regulator, reactor, binder and igniter were identified as required ancillaries (Table 1). System integration issues, ignition mechanisms and burn kinetics were discussed as areas of needed research/resources (Table 4).

Carbon-Based Storage Materials
Fullerenes- Carbon molecular species C_{60} and C_{70}, and other related closed-cage compounds collectively known as fullerenes, can be chemically hydrogenated at temperatures near 400°C with H_2 and elevated pressures. Fullerenes are currently synthesized by several methods including arc-discharge with an anticipated future cost of $25/kg for large-scale production. A containerless storage density of 7.7 wt% is a theoretical maximum corresponding to a stoichiometry of $C_{60}H_{60}$, while a density of 6 wt% has been experimentally achieved with a H_2 pressure of 3500 psi at 350°C (Table 1). Future goals in this area include reduction of the hydrogenation pressure

and the hydrogenation/dehydrogenation temperatures. These reactions may be facilitated through the use of catalysts and the inclusion of solvents. Scale-up of production is a focal point for future work, as is system integration (Table 4). Integration issues include the need for a heater to liberate H_2 and the need for remote H_2 recharging.

Single Wall Nanotubes- Single wall carbon nanotubes are relatives of the fullerene-family of carbon nanostructured materials. They consist of individual curved sheets of graphite which are seamlessly joined to form cylinders with diameters of 1 to 2 nm. These structures are currently grown in high-yield (~90%) using laser vaporization techniques, but can also be produced with other methods. The ends of the tubes are normally capped by fullerene hemispheres which can be removed by oxidation. Once opened, hydrogen can diffuse into and condense within the interiors of the nanotubes at room temperatures. The binding energy for hydrogen is ~ 5 times higher inside the tube than for H_2 adsorbed on a graphitic plane.

Theoretical storage densities are a function of nanotube diameter and range between 2 and 5 wt% without considering a container (Table 1). Experiments on powders containing small quantities of nantotubes indicate storage densities between 5 and 10 wt% on a nanotube weight basis. Scale-up of nanotube synthesis is being pursued in numerous laboratories and advances will be necessary for nanotubes to become a viable H_2 storage option. Since the material acts as a sponge for H_2, heat management is not expected to be a problem and storage pressures will be low. A supply of H_2 at a relatively low pressure (e.g. 100 psi) will be required for refueling.

Graphite Nanofibers- Graphite nanofibers are grown by the decomposition of a gaseous mixture of C_2H_2/CO on a metal catalyst particle at temperatures around 600°C. Carbon deposited on one side of the particle, diffuses through the metal and precipitates as platelets of graphite on the opposite side of the particle. It is proposed by the inventors that hydrogen diffuses into the fibers, between the graphite platelets, rapidly and effectively by a capillary condensation process. It is claimed that up to 50 wt % (Table 1) hydrogen can be absorbed by the fibers by exposing them to several hundred atmospheres of hydrogen for 24 hours. Recovery of 80-85% of the hydrogen is reported to occur upon reduction of the pressure to near atmospheric conditions. The remaining 15% is said to be recoverable by heating to over 500°C. (The hydrogen loading and release properties have not been reported in peer reviewed literature). If the hydrogen storage yields (50 wt %) are valid, then this material represents by far the best option for hydrogen storage, implying an incredible association of 12 hydrogen atoms per carbon atom in a non-chemically bound state. Other issues identified include production scale-up, surface treatment and understanding the effect of contaminants (Table 4).

Table 4: Evaluation

Technology	Time to implementation Short = 1-3 years Med = 3-5 years Long = 5+ years	Research/Resources Needed	Probability of Success for Stated Applications Likely Possible Not Likely
Pressurized tanks (1.5 safety factor @300 K)	Short	Full metallized polymer bladder, light weight hardware	Likely
Glass bubbles on film roll @9000 psi	Medium	Bubble scale-up, batch high-pressure filling, H_2 release mechanism	Likely
Low-temperature metal hydride	Short		Likely
High-temperature metal hydride (Mg-23% Ni with thermite)	Short	Catalysts, thermite	Likely
$NaAlH_4$ (with water)	Short		Likely
AlH_3 (with air)	Short	Ignition, kinetics	Likely
Fullerene	Medium	Production scale-up	Possible
Single wall nanotubes	Long	Production scale-up, effect of contaminants	Possible
Graphite nanofibers	Short	Production scale-up, surface treatments, effect of contaminants	Likely

Table 5. Comparative Aspects.

Rankings: 3 = Significant issue; 2 = Moderate issue; 1 = Small issue; 0 = Not Applicable.

TECHNOLOGY	Pressurized tanks	Glass Bubbles	Low-temperature metal hydride	High-temperature metal hydride (Mg-23% Ni)
1. Shelf life/ stability under storage	1	1	0	0
2. Response time/ load following	0	0	0	1
3. Start- Stop flexibility and response time	1	0	0	2
4. Safety	3	1	0	1
5. Reload time	0	0	0	0
6. Environmental restraints (operating T range; air quality required; orientation sensitivity; recyclable or disposable)	1	0	0	1
7. System integration constraints (Thermal match to fuel cell; water balance; parasitic power requirement)	0	1	1	1
8. Thermal signature	0	0	0	1
9. Manufacturability	1	3 (filling)	0	0
10. Cost	1	1	1	1
11. Refueling	3	NA	1	1

Table 5 (continued). Comparative Aspects.

Rankings: 3 = Significant issue; 2 = Moderate issue; 1 = Small issue; 0 = Not Applicable.

TECHNOLOGY	NaAlH$_4$ / AlH$_3$	Fullerenes	Single wall nanotubes	Graphite Fibers
1. Shelf life / stability under storage	0/1	0	0	1
2. Response time/ load following	0/1	1	0	0
3. Start- Stop flexibility and response time	1/1	2	0	0
4. Safety	1/1	1	0	0
5. Reload time	0/0	0	0	0
6. Environmental restraints (operating T range; air quality required; orientation sensitivity; recyclable or disposable)	1/0	1	1	2
7. System integration constraints (Thermal match to fuel cell; water balance; parasitic power requirement)	1/2	1	3 (release pressure)	1
8. Thermal signature	0/0	1	0	0
9. Manufacturability	0/0	3	3	2
10. Cost	1/1	3	3	1 – 2
11. Refueling	NA/NA (reactor reusable)	3 (high T and P)	0	2 - 3
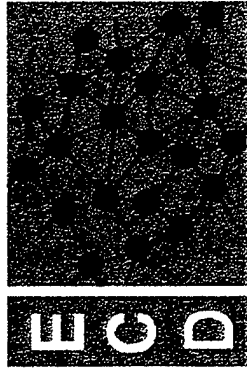
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Metal Hydride Hydrogen Storage

for

Small Portable Power Systems

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ENERGY

Generation

Storage

Photovoltaics

United Solar	U.S. JV w. Canon Corp.
Sovlux	JV w/ KVANT/MINATOM
Canon	Licensee in Japan
U.S. DOE	PV: BONUS Program
U.S. DOE	R and D Contract

□ Solar Roofing Products
□ Remote Power Applications
- home lighting
- water pumping
□ Consumer Products
- battery chargers
- portable electronics
- marine
□ Telecommunications
□ Grid-connected - Distributed Power
□ Centralized Power Generation

Battery

□ Ovonic Battery Licensees:

Matsushita	Sovlux
Hitachi-Maxell	Walsin
Gold Peak	Gates Energy
Samsung	Harding Energy
Varta Batterie	Daido Steel
Eveready	Furukawa
Duracell	

Three Other Major Japanese
Battery Manufacturers

□ Electric Vehicle Batteries

GM Ovonic	EV Battery Mfg. JV
USABC	Development Contract
APIC	Licensee
Hyundai	Licensee
Sovlux	JV w/ KVANT/MINATOM
Gold Peak Ind.	Licensee
Honda	Customer & Shareholder
Saft	Licensee

□ Electric Motorcycles & Scooters

Walsin	Licensee
Sanoh	Licensee
Sovlux	JV w/ KVANT/MINATOM
Sanoh/Ovonic	Joint Venture

□ Utility/Residential Storage
□ NASA/Telecommunications

Optical Memory

Licensees:

Panasonic	Toshiba
Plasmon	Polaroid
Toray	Sony
Asahi Chemical	IBM
Hitachi	

Microelectronics

Development program for
thin-film non-volatile
semiconductor memory devices

□ DRAM
□ Flash EEPROM
□ Universal Memory
□ Neural Networks
□ N^{th}-gen Computer
□ Thin-Film Logic
□ Thin-Film AMLCD pixel addressing
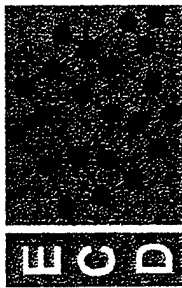
Materials and Manufacturing Technology

Materials development, design and fabrication of pilot line and production equipment for
licensees and other strategic partners including United Solar, GM Ovonic, etc.

ECD

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E C D

Energy Conversion Devices, Inc.
1675 West Maple Road
Troy, MI 48084
Telephone: 810/362-4780
FAX: 810/362-0012

Technology: **Metal Hydrides**

Strengths:

- Over 15 years experience developing and optimizing metal hydrides for various applications;

- Large-scale manufacturing capabilities;

- Multiple production technique capabilities-
  - High temperature melt techniques,
  - Rapid quench techniques,
  - Mechanical alloying techniques,
  - Thin film technologies;

- Patented and proprietary technologies-
  - high density powder bed packing techniques,
  - high hydride bed thermal conductivity,
  - modular designs – adaptable capacities;

Contact: Dr. Krishna Sapru
               Director, Thermal Hydrides and Thermoelectrics

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Energy Conversion Devices, Inc.
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High Density and Safe Hydrogen Storage for Unmanned Undersea Vehicles and Electric Land Vehicles

DARPA SBIR Phase II Project
Contract No. DAAH01-95-C-R150

Development of a prototype hydrogen storage device utilizing advanced Mg-based metal hydrides with > 5 wt. % (H/M) storage capacity. Heat for the hydrogen desorption supplied by combustion of a portion (~31%) of the stored hydrogen.

Dehydriding Kinetics at 350°C
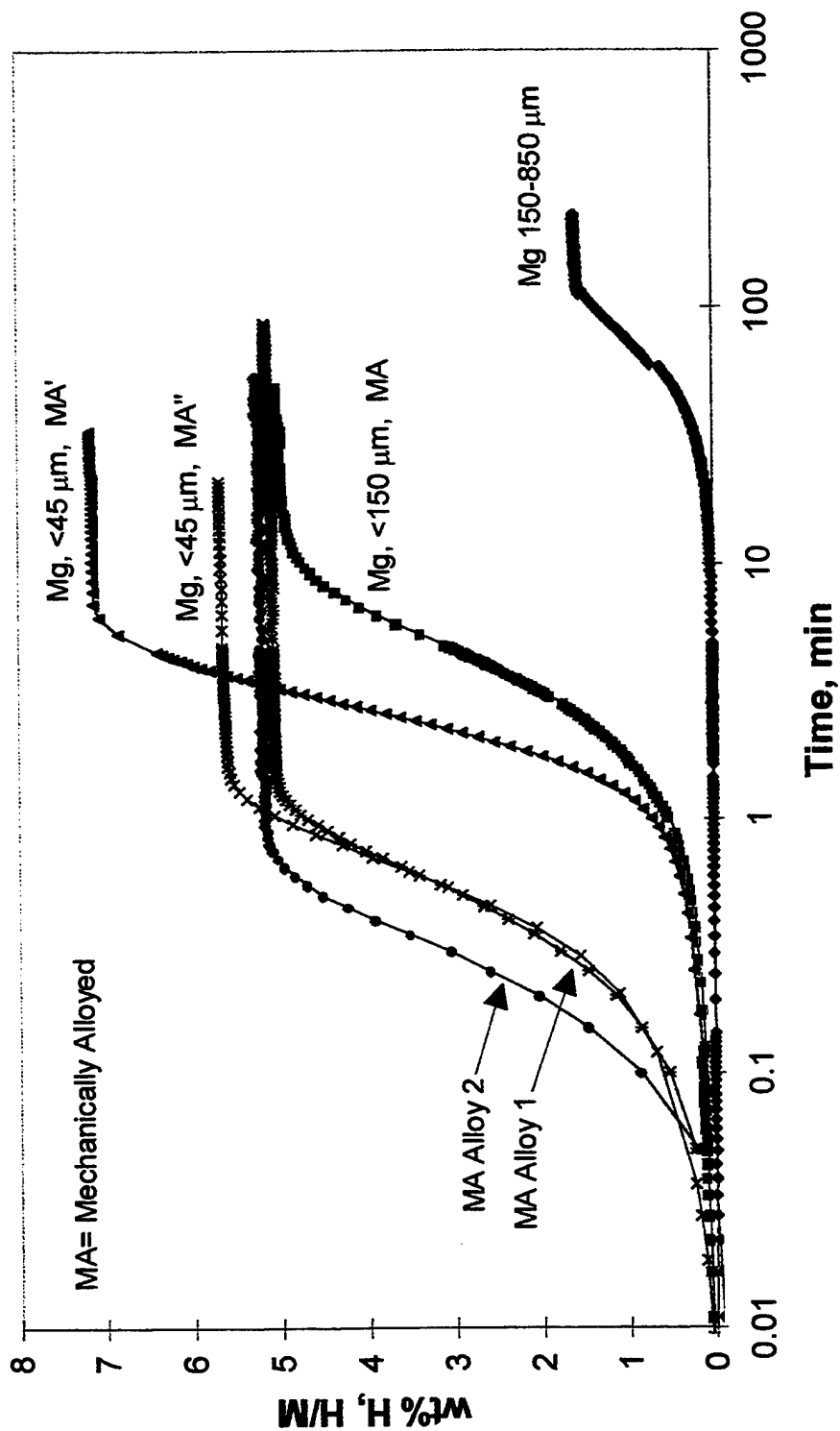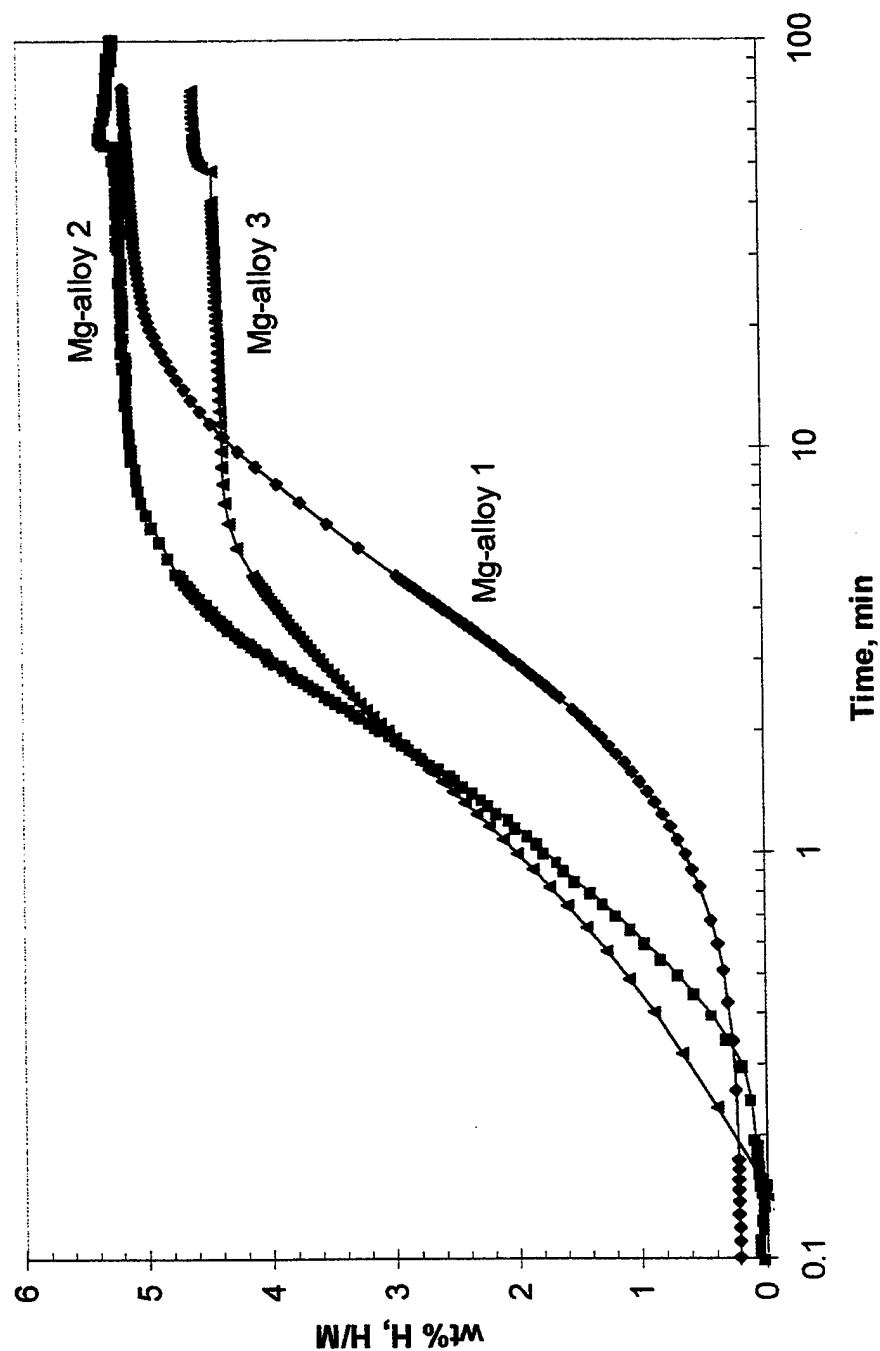
MA= Mechanically Alloyed

Mg, <45 μm, MA'

Mg, <45 μm, MA"

Mg, <150 μm, MA

Mg 150-850 μm

MA Alloy 2

MA Alloy 1

wt% H, H/M

Time, min

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300°C Dehydriding Kinetics
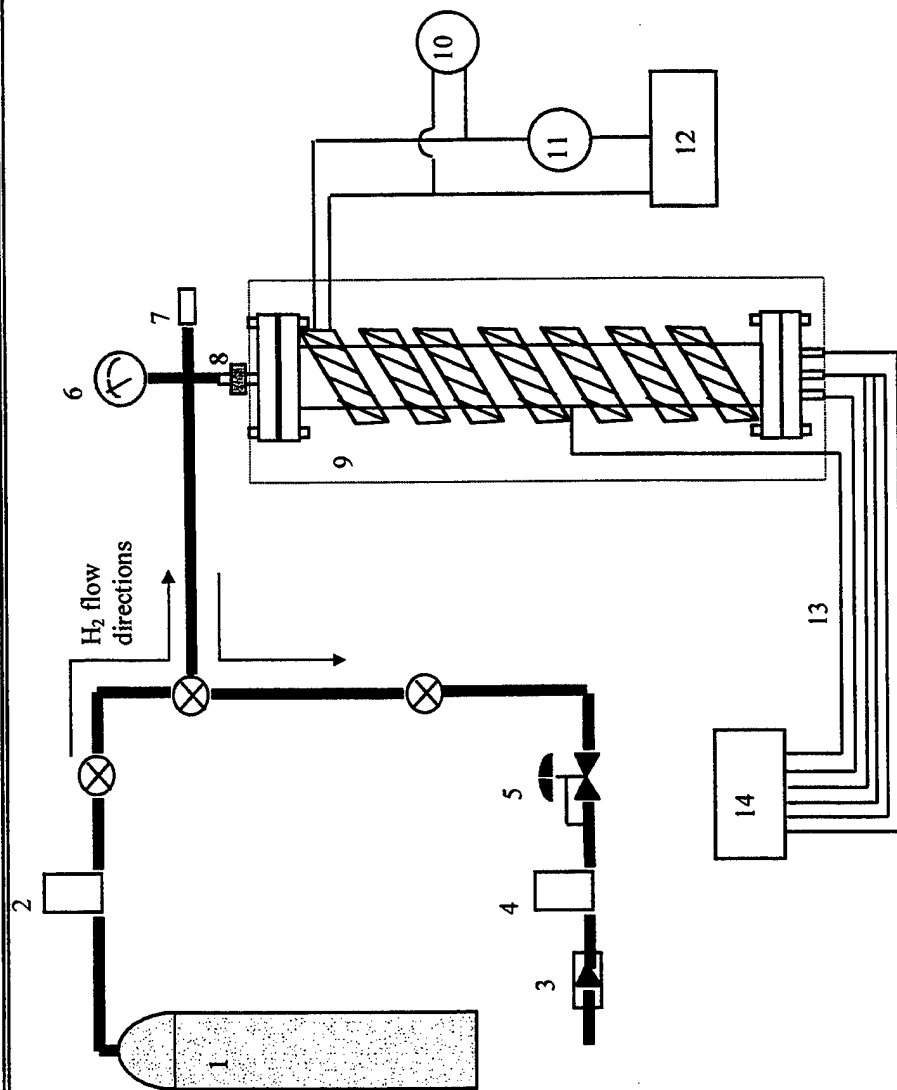
Schematic of Mg-based hydride hydrogen storage test module.

Legend: 1- Hydrogen cylinder; 2- 10000 sccm flow controller; 3- 5 psig check valve; 4- 1000 sccm flow controller; 5- pressure regulator; 6- pressure gauge; 7- pressure relief valve; 8- 2 μm filter; 9- insulted SS tube with heat tape; 10- voltage meter; 11- current meter; 12- variac power source; 13- thermocouples; 14- multiple input digital temperature meter
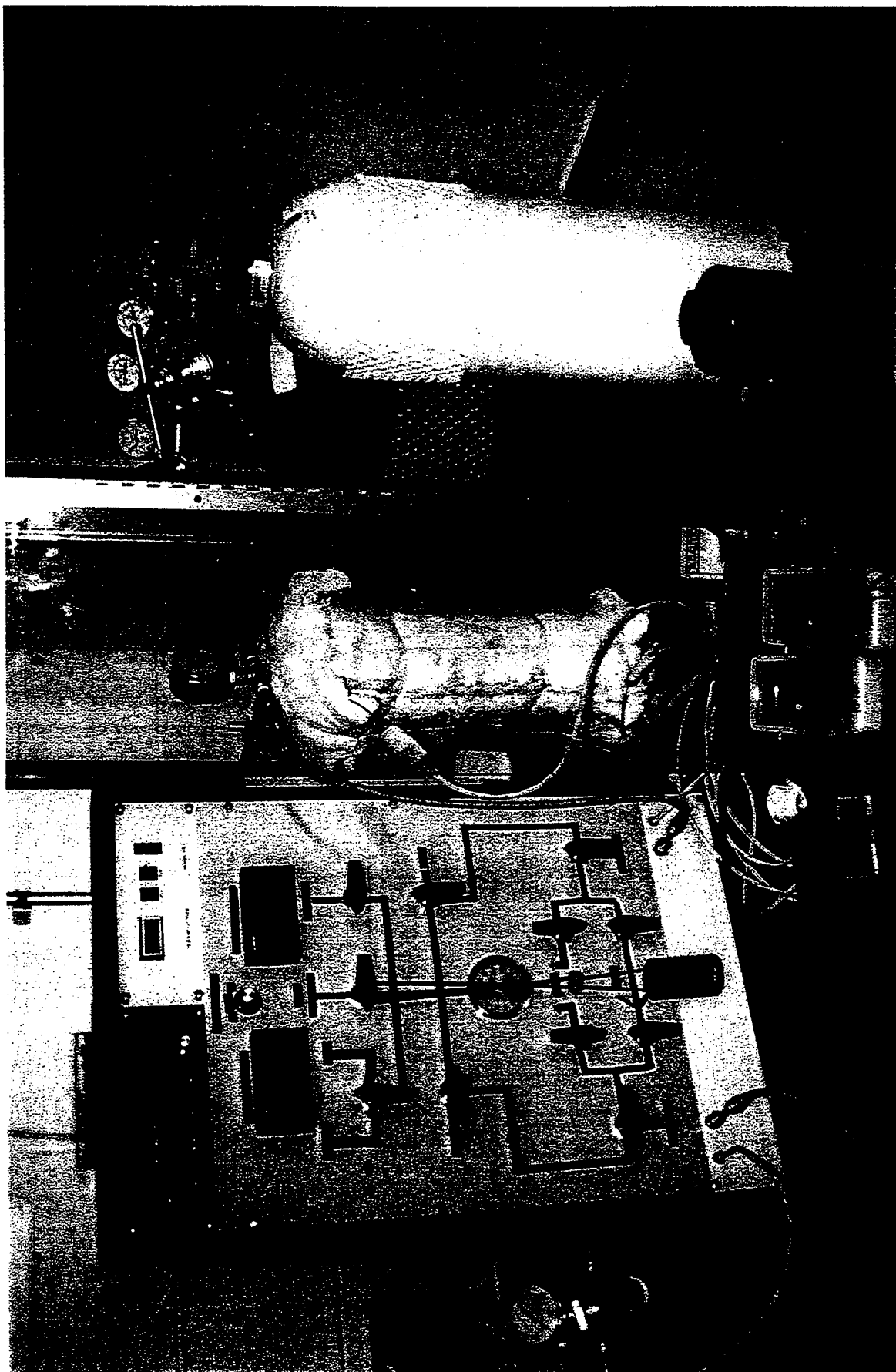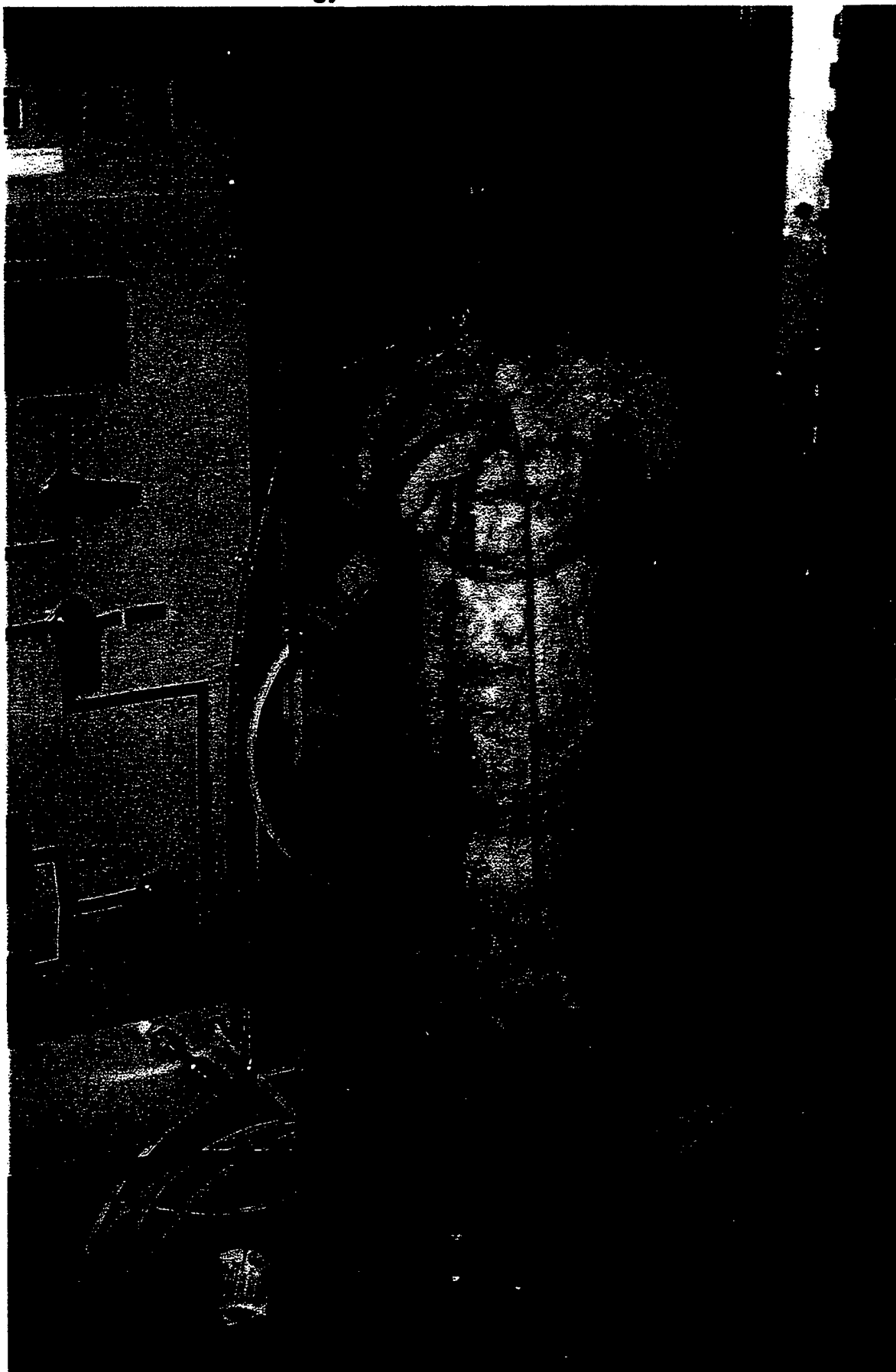
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Mg-based Alloy Prototype Test Module

Gas discharged and temperature vs. Energy input; discharge rate of ~750 sccm H_2
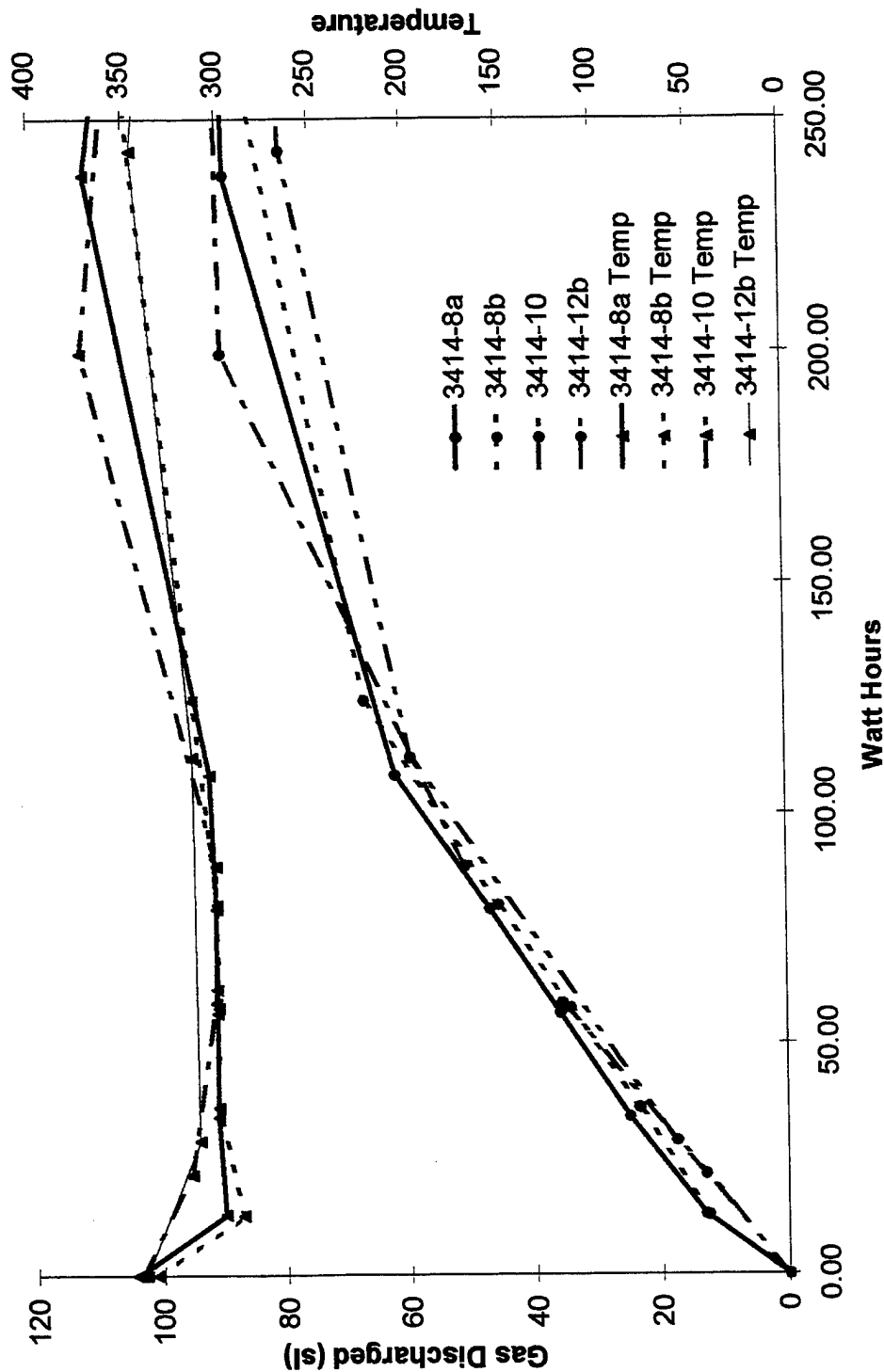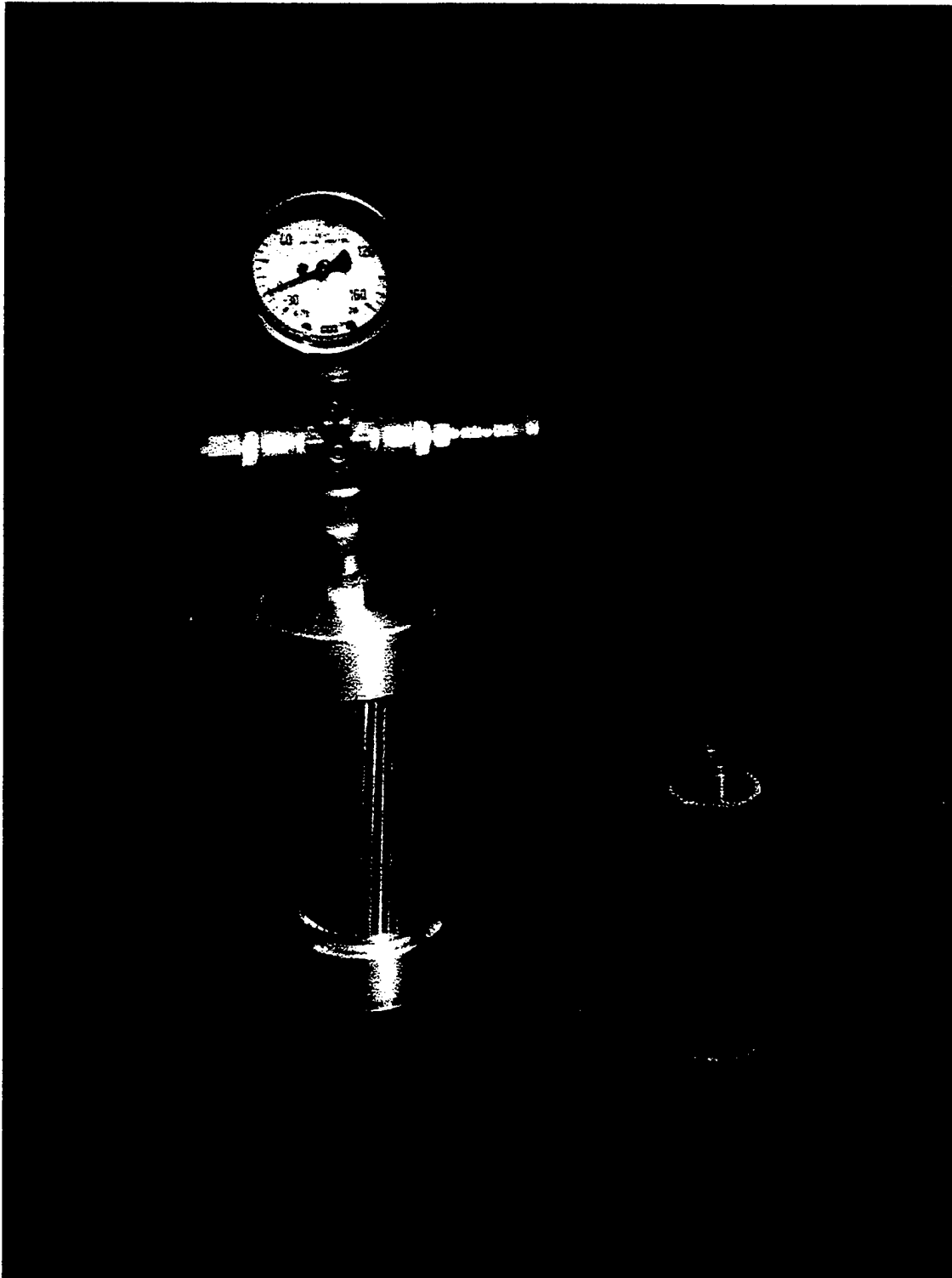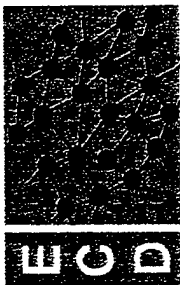
Energy Conversion Devices, Inc.
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Troy, MI 48084
Telephone: 810/362-4780
FAX: 810/362-0012

Hydrogen Desorption of a 100 standard liter prototype canister

300 sccm discharge rate, submerged in water bath
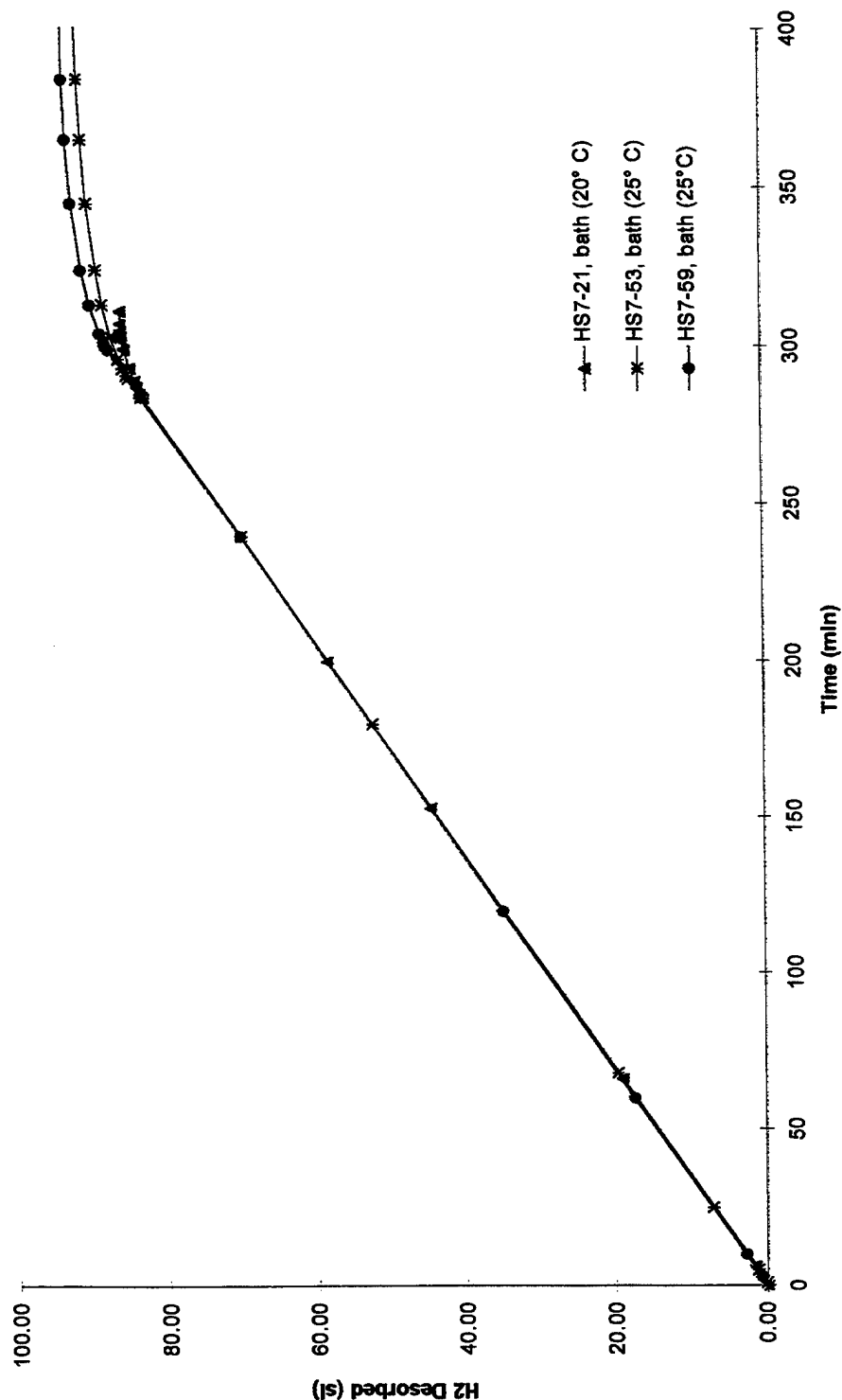
HYDROGEN STORAGE IN METAL HYDRIDES

Ricardo B. Schwarz
Center for Materials Science, Mail Stop K765
Los Alamos National Laboratory
Los Alamos, NM 87545

Summary of the Presentation:

We describe an integrated hydrogen storage systems consisting of a
hydrogen storage medium and a heat delivery system (needed to
activate the release of the hydrogen). The hydrogen is stored in a
magnesium-nickel alloy prepared by mechanical alloying (a high-
energy ball milling technique). The heat needed for the hydride
decomposition is provided by a *thermite* powder which burns at a
controlled rate when exposed to air. The hydride and thermite are
contained inside concentric thin-wall stainless steel tubes. The
thermite is located in the inner tube. The hydride is located between
the inner and outer tubes. This way, all the heat delivered by the
thermite is used by the hydride. The hydride stores 5.5 weight
percent hydrogen.

PROGRAM GOALS:

DESIGN A SELF-CONTAINED HYDROGEN DELIVERY SYSTEM
WITH THE FOLLOWING CHARACTERISTICS:

1. GRAVIMETRIC DENSITY > 600 Wh / kg

2. VOLUMETRIC DENSITY > 1200 Wh / liter

3. SYSTEM ENERGY STORAGE 1.3×10^6 Wh

SELECTED APPROACH

HYDROGEN DELIVERY FROM LIGHT METAL HYDRIDE

ENTHALPY OF DECOMPOSITION: THERMITE OXIDATION
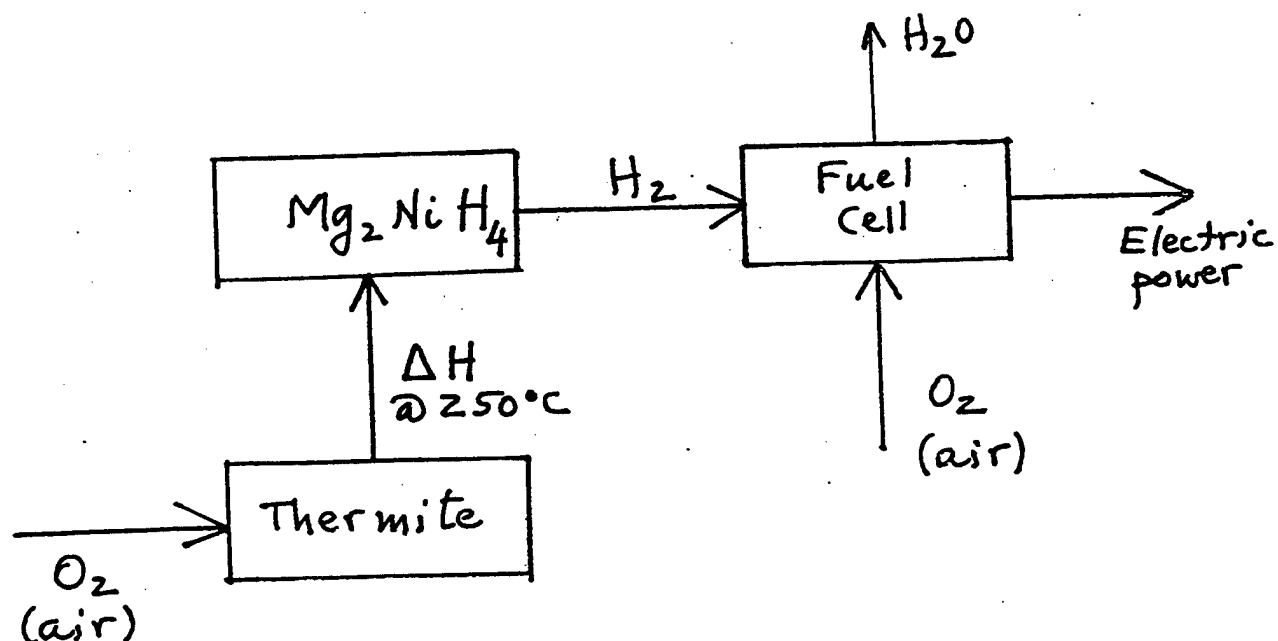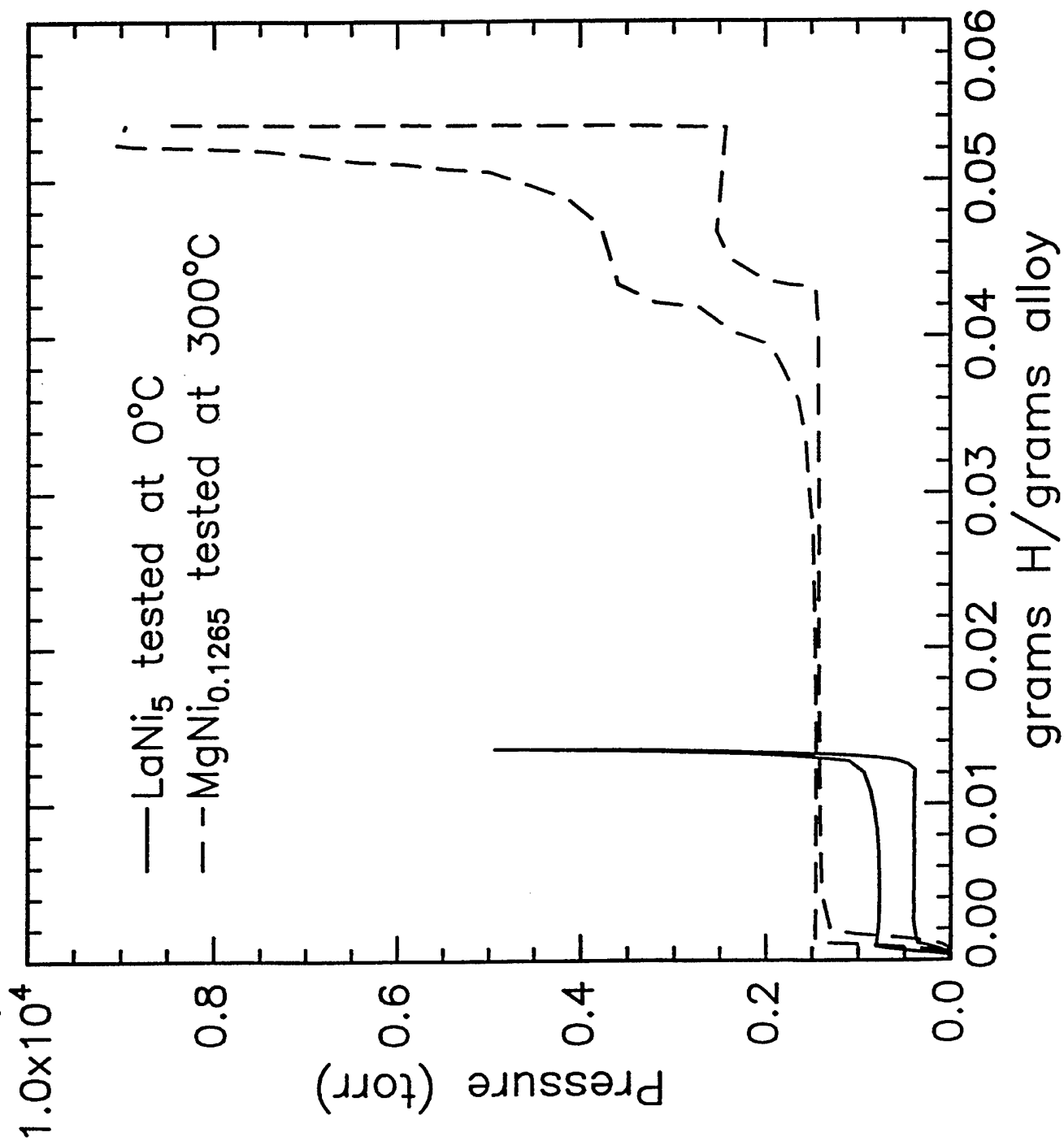
Figure 6

TESTING SETUP FOR INTEGRATED HYDROGEN DELIVERY SYSTEM

HYDROGEN OUT

FLOW
METER

THERMITE
CELL

HYDRIDE
CELL

PRESSURE
GAUGE

THERMOCOUPLES

IEEE-488

MULTICHANNEL VOLTMETER

COMPUTER

FLOW
METER
AND
CONTROL

AIR
SUPPLY

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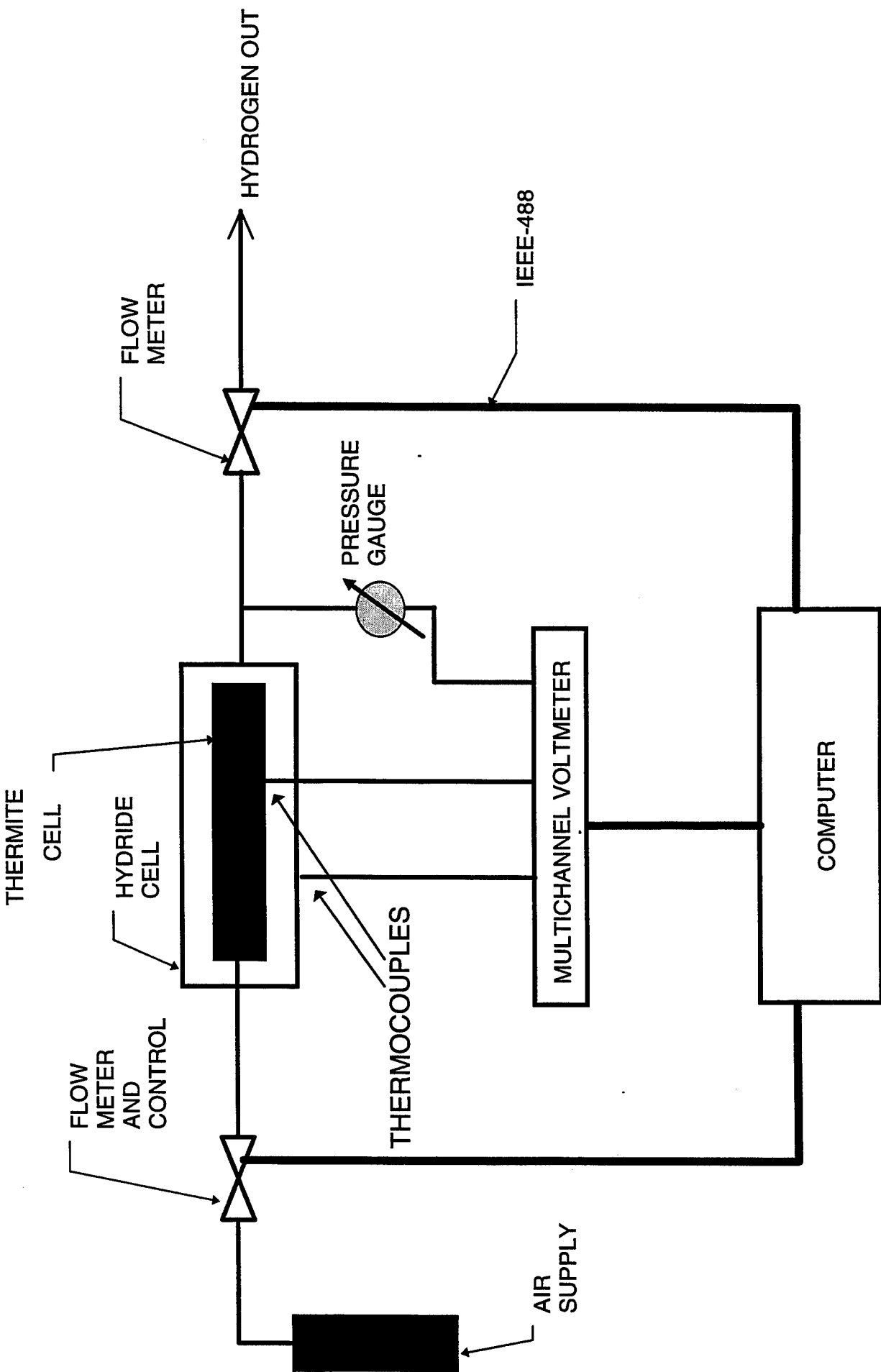
CONCLUSIONS

- Nanosized two-phase mixtures of Mg and Mg_2Ni prepared by mechanical alloying (MA) stores 5.4 weight percent hydrogen

- Alloy powder $Mg_{60}Si_{40}$ (at %), also prepared by MA, burns in air, delivering 18 kJ/g

- Modeling of the concentric hydrogen delivery system indicates that it should deliver:

  851 Wh / kg   (142 % of specifications)

  1087 Wh/lt   (91% of specifications)

CURRENT WORK

- Testing of Cell performance

- Design electronic feedback system (computer controlled; can be integrated into a chip)

- Research alternative thermite alloys materials

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Hydrogen Storage in Fullerenes

Materials & Electrochemical Research (MER)

Corporation

Tucson, Arizona

Principle of Hydrogen Storage Using Fullerenes

- Hydrogen charge and discharge to/from fullerenes is achieved by fullerene hydrogenation and dehydrogenation processes.

$$C_{60} + \frac{x}{2} H_2 \Leftrightarrow C_{60}H_x \qquad x = 2-54$$

- The advantages of hydrogen-fullerene system are the high storage capacity (up to 7% by weight), stable at ambient conditions, and non-toxic.

-----MER Corporation, Tucson, AZ-----

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Fullerene Hydrogenation and Dehydrogenation

- Hydrogenation can be achieved by high temperature and pressure process to form fullerene hydrides, $C_{60}H_{48}$. This product is stable in ambient condition.

- Dehydrogenation can be achieved by heating fullerene hydride $C_{60}H_x$ to 350 to 425°C temperature.

- 57.9 kJ/mole H_2, or 20% of hydrogen heating value is required for dehydrogenation.

-----MER Corporation, Tucson, AZ-----

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Hydrogen Storage Capacities Based On Fullerene Hydrides Considering Energy Balance

wt%	5.0 ($C_{60}H_{48}$--6.25%)
kg/m^3	73.1
mAh/gm	1353
mAh/cc	2272
Wh/kg	943
Wh/l	1590
wt for 430KWh	455 kg
volume for 430KWh	271 liter

-----MER Corporation, Tucson, AZ-----

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Theoretical Capacities–Orlando Meeting Format

gravimetric density	6.25%
volumetric density	91.4 kg/m^3
Ah/kg	1,691
Wh/kg	1,031
Wh/L	1,739
thermal burden	57.9 kJ/mole H$_2$

-----MER Corporation, Tucson, AZ-----

Theoretical Capacities-Orlando Meeting
Format-Cont'd

Wt for a 300W, 10kWh	8.53 kg
Vol. for a 300W, 10kWh	5.69 liter
Wt for a 100W, 1kWh	.0.853 kg
Vol. for a 100W, 1kWh	0.569 liter
Wt for a 10W, 90kWh	76.77 kg
Vol. for a 10W, 90kWh	51.21 liter

-----MER Corporation, Tucson, AZ-----

Conclusions

- It is demonstrated that high hydrogen storage capacity can be achieved using fullerene hydrides.

- Although thermodynamically feasible to dehydrogenate hydrogen from fullerene hydrides at moderate temperatures (~100°C), certain limitations must be overcome before it can be achieved experimentally (Now being investigated under DARPA program). However, hydrogen release can be achieved around 400°C.

- The key issue is to develop a practical method to supply the heat for H_2 release (e.g..., Los Alamos approach)

-----MER Corporation, Tucson, AZ-----

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WORKING GROUP 2: Chemical Hydrides

CHEMICAL HYDRIDES AND RELATED MATERIALS

The participants in Session 2 were:

Oliver Murphy, Chair	Lynntec
Omourtag Velev, Scribe	Texas A&M University
Deryn Chu	U.S. Army Research Laboratory
Ottmar Dengel	Royal Systems
Raouf Loutfy	MER Corporation
Michael Matthews	University of South Carolina
Subash Narang	SRI
Roger Pyon	PRC
Ron Akers	Dismounted Battle Lab
Otto Adlhart	A.F. Sammer
Werner F. Beckert	Royal Systems
Darren Browning	Defense Research Agency
Tom Feldman	Hysorb Technologies
Bob Hamlen	U.S. Army Research Laboratory
Craig Jensen	University of Hawaii
William Kaska	UC Santa Barbara
Gary Mepsted	Electrochemical Power Sources
Bob Nowak	DARPA
Darlene Slattery	Florida Solar Energy Research
Walter Taschek	A.F. Sammer Consultant
John Wilkes	U.S. Air Force Academy

As part of the Hydrogen Storage and Generation Workshop, Working Group 2 was charged with assessing and evaluating chemical hydrides and related materials to determine their suitability as sources of hydrogen for small fuel cell power sources. The technologies considered by this Working Group, under the general title Chemical Hydrides and Related Materials, are listed below. Material characteristics and estimates of weight and volume for each technology are outlined in Tables 1 and 2, Executive Summary. Tables 6-8, in which evaluation of the technologies, comparative aspects and systems issues are summarized, are presented at the end of this report.

- Silanes-Boranes/Hydrolysis

- Solid State Chemical Hydrides

- Cycloalkanes/Dehydrogenation

- Classical Hydrides/Hydrolysis

During the first day-and-a-half of the Workshop, presentations on each of the technologies identified in this list were made to all the Workshop participants by experts actively working in each area of technology. After extensive deliberations during the afternoon of the second day,

the findings, conclusions, and recommendations of Working Group 2 were presented to all the Workshop participants on the third day of the Workshop. These are discussed in the following section.

Findings, Conclusions, and Recommendations of Working Group 2

Material characteristics for the various technologies considered are outlined in Table 1. The theoretical hydrogen yield (kg H_2/kg Materials) varied from 0.073 for classical hydrides/hydrolysis and cycloalkanes/dehydrogenation, to 0.1 for silanes-boranes/hydrolysis and solid state chemical hydrides. The Ah/kg materials and Wh/kg materials (at 0.7 V) varied in a similar manner. In terms of Wh/L materials (at 0.7 V), the solid state chemical hydrides yielded the highest value at 1876 while the classical hydrides/hydrolysis gave rise to the smallest value, 460. Thus, in terms of available energy density, the classical hydrides/hydrolysis are the least attractive.

Although indicated as occurring at room temperature, technologies involving hydrolysis will react even more readily at elevated temperatures. Addition of a small amount of an alcohol to water would facilitate hydrolysis reactions taking place even at temperatures well below the normal freezing point of pure water. While the solid state chemical hydrides would yield hydrogen at any temperature, the cycloalkanes/dehydrogenation would yield hydrogen only upon being heated in the presence of a catalyst at temperatures in the range 150 - 250°C. Of the technologies considered, only the cycloalkanes/dehydrogenation were endothermic. The required ancillaries for solid state chemical hydrides would include a holding tank capable of storing H_2 gas at high pressure (2000 psi) while the cycloalkanes/dehydrogenation would need a H_2 gas permeable membrane. For three of the technologies, thermal management is an issue that needs to be addressed.

Estimates of weight and volume for each technology for three specific missions or applications (300 W, 10 kWh; 100 W, 1 kWh; and, 10 W, 90 kWh) are presented in Table 2. Based on this analysis, the silanes-boranes/hydrolysis appear to be the most attractive. However, as shown in the table, the range of estimates for the other technologies is small.

Each of the technologies was evaluated in order to determine the time required to demonstrate a prototype system in the field, the research/resources needed, and the probability of success for specific missions or applications. The results of this evaluation are presented in the Executive Summary and also in Table 6. For both the 300 W, 10 kWh, and the 100 W, 1 kWh applications, the time for implementation of each technology was considered to be short (1-3 years). However, for the 10 W, 90 kWh application, the time for implementation was viewed as being at least medium (3-5 years). The research/resources needed to implement each technology are identified in the table. An important and attractive feature of the cycloalkanes/dehydrogenation technologies is that they are the only truly recyclable technology of those considered by the Working Group. The probability of success for each technology for the stated applications is also given in Table 6.

Various parameters associated with each technology were compared and ranked on a scale of 0 - 3, where 0 equals not applicable, 1 equals small issue, 2 equals moderate issue, and 3 equals significant issue. The results of this analysis are presented in Table 7. For all technologies, two parameters ranked moderate-to-significant; these were safety and thermal signature. Because of the extreme sensitivity of state-of-the-art infrared sensors, the thermal signatures associated with the technologies may be overly stated, particularly when compared with heat en-

gine-based power sources. Similarly, the safety aspect of the technologies must be put in perspective with other electrical power sources used by the Army, e.g., the lithium/sulfur dioxide primary battery. The latter battery system must be carefully handled when in use and when being disposed. Aspects of the technologies of moderate issue were response time/load following capabilities, environmental restraints, and system integration constraints. Cost varied over the whole ranking range, depending on the maturity of the technology considered.

Systems issues for the various technologies evaluated are presented in Table 8. Three of the technologies are, in principle, capable of operating over a wide temperature range (-40 - +75°C) on using an appropriate design. The fourth technology operates only at elevated temperatures, most suitability in the range 150 - 250°C. However, the latter technology is the only one that is truly recyclable and has a built-in safety feature in that it can only produce hydrogen at low hydrogen gas pressures. As stated earlier, three of the technologies give rise to exothermic thermal loads that range from low to high while the fourth technology is endothermic. The two hydrolysis-based technologies involving either silanes-boranes or classical hydrides give rise to user defined hydrogen gas pressures on producing hydrogen. In contrast, the solid state chemical hydrides yield high hydrogen gas pressures (approximately 2000 psi) and the cycloalkanes/dehydrogenation are low pressure (less than 60 psi) systems.

Table 6: Evaluation

Technology	Time to implementation Short = 1-3 years Med = 3-5 years Long = 5+ years	Research/Resources Needed	Probability of Success for Stated Applications Likely Possible Not Likely
Silanes-Boranes/ Hydrolysis	Short-Medium	Thermal and Kinetic Data, System Design, Synthesis	Likely for all Three Applications
Solid State Chemical Hydrides	Short-Medium	System Design for Long Duration Missions, Synthesis for More Energetic Systems, Thermal Management	Likely for Applications 1 and 2 Possible for Application 3
Cycloalkanes/ Dehydrogenation	Short-Medium	H_2 Permeable Membrane, Catalysts, Cyclability, System Design, Thermal Management	Likely for all Three Applications
Classical Hydrides/ Hydrolysis	Short-Medium	System Design, Thermal Integration, Control, Ligand Chemistry, Synthesis	Likely for Applications 1 and 2 Possible for Application 3 Ligands - Possible

Table 7. Comparative Aspects

Rankings: 3 = Significant issue; 2 = Moderate issue; 1 = Small issue; 0 = Not Applicable

Technology	Silanes-Boranes/ Hydrolysis	Solid State Chemical Hydrides	Cycloalkanes/ Dehydrogenation	Classical Hydrides/ Hydrolysis
1. Shelf life/stability under storage	2	1	0	1
2. Response time/load following	2	0	2	2
3. Flexibility in use (ease of stop/start; number of cycles; cycle speed)	1	0	3	2
4. Safety	3	2	2	3
5. Recharge time	0	0	1	0
6. Environmental restraints (operating T range; air quality required; orientation sensitivity; recyclable or disposable)	2	0	2	2
7. System integration constraints (Thermal match to fuel cell; water balance; parasitic power requirement)	2	0	2	2
8. Thermal signature	1	3	3	3
9. Manufacturability	3	1	1	1
10. Cost	3	1	2	3

Technology	Start-up Temperature Range, °C	Thermal Load	Operating Pressure	Recyclability
Silanes-Boranes/ Hydrolysis	-40 - +75	Exothermic Low	User Defined	No
Solid State Chemical Hydrides	-40 - +75	Exothermic High	High Pressure	No
Cycloalkanes/ Dehydrogenation	150 - 250	Endothermic ?	Low Pressure	Yes
Classical Hydrides/ Hydrolysis	-40 - +75	Exothermic High	User Defined	No

Technology	Reactant 1	Reactant 2	Reactant 3	Product 1	Product 2
Silanes-Boranes/ Hydrolysis	Liquid	Liquid	N/A	Gas	Liquid/Solid
Solid State Chemical Hydrides	Solid	Solid	N/A	Gas	Solid
Cycloalkanes/ Dehydrogenation	Liquid	N/A	N/A (Catalyst)	Gas	Liquid/Solid
Classical Hydrides/ Hydrolysis	Solid	Liquid	N/A	Gas	Solid

Table 8. Systems Issues for Chemical Hydrides and Related Materials

For the four technologies evaluated, the reactant and product phases are identified. In each case, the primary and desired product is hydrogen gas. For the silanes-boranes/hydrolysis, the reactants are in the liquid phase while the byproducts can be either in the liquid or solid phase. In the case of the solid state chemical hydrides, the reactant mass consists of well mixed solid powders that yield solid byproducts upon reaction. The cycloalkanes are liquids that undergo a dehydrogenation reaction in the presence of either a homogeneous or heterogeneous noble metal-based catalyst. The byproduct formed can be either a liquid or a solid that can readily be rehydrogenated. Reactants in the case of the classical hydrides/hydrolysis are usually a solid (the hydride) to which a liquid (water) is added in a controlled manner. The byproduct formed is a hydrated oxide or oxyhydroxide.

John Wilkes, Air Force Academy contribution to group 2 discussions

Table 1: Material Characteristics

Technology	Theoretical H_2 yield (kg H_2/kg materials)	Ah/kg materials	Wh/kg materials (at 0.7 V)	Wh/L materials (at 0.7 V)	Thermal Burden kJ/kg H_2	Required Ancillaries
Liquid H_2	1	2.659×10^4	1.861×10^4	1.30×10^3	+4408	
LiAlH$_4$	0.2125	5.650×10^3	3.955×10^3	3.401×10^3	-6.246×10^4	1.8 kg/kg H_2
other chem hydride	>0.2125	$>5.650 \times 10^3$	$>3.955 \times 10^3$	$>3.401 \times 10^3$	-7.721×10^4	1.8 kg/kg H_2
LiBH$_4$	0.06714	1.785×10^3	1.249×10^3	1.428×10^3	-3.64×10^4	1.8 kg/kg H_2

Table 2: Mission-Specific Estimates

Technology	Est. wt. (kg) for a 300 W, 10 kWh system	Est. vol. (L) for a 300 W, 10 kWh system	Est. wt (kg) for a 100 W, 1 kWh system	Est. vol. (L) for a 100 W, 1 kWh system	Est. wt. (kg) for a 10 W, 90 kWh system	Est. vol. (L) for a 10 W, 90 kWh system
LiAlH$_4$	5.4 kg					
other chem hydride	<5.4 kg					
LiBH$_4$	13.8 kg					

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Table 3: Evaluation

Technology	Time to Implementation short = 1.3 years med. = 3.5 years long = 5+ years	Research / Resources Needed	Probability of Success for Stated Applications: Likely Possible Not likely
LiAlH$_4$	short	- Thermal decomposition and control - Cost reduction - Contamination / purity	Possible
other chem hydride	short	- Synthesis scale-up - Cost reduction - Rate of reaction	Likely
LiBH$_4$	short	- Cost reduction - Rate of reaction	Possible

Table 4: Hydrogen Storage Densities

Form	Example	Hydrogen Density g_{H_2} / cm^3
Gas	H$_2$(g), P = 1 atm, t = 20 °C	0.0008987
Gas	H$_2$(g), P = 2000 psi, t = 20 °C	0.0098
Gas	H$_2$(g), P = 14,000 psi, t = 20 °C	0.048
Liquid	H$_2$(l), P = 1 atm, t = 254 °C	0.070
Solid	H$_2$(s), P = 7 kPa, T = 13.8 K	0.087
Metal Hydride	PdH$_2$	0.0503
Metal Hydride	TiH$_2$	0.156
Chemical Hydride	LiAlH$_4$	0.193
Chemical Hydride	LiBH$_4$	0.252
Metallic	H, P = 1.4 Mbar, T = 3000 K	0.5
Graphite Inclusion	H$_2$/C(gr) nanofibers	6.12

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Hydrogen Storage via Reversible Cycloalkane
Dehydrogenation Catalyzed by PCP Pincer Complexes

Craig M. Jensen, Departement of Chemistry , University of Hawaii

A major concern in the development of hydrogen as a fuel is the problem of hydrogen storage. Solid hydrogen storage systems based on metal hydrides are safer and require far less volume than either high pressure or cryogenic storage systems. However, hydrides of metals and alloys which reversibly release hydrogen at adequate rates contain too low of hydrogen weight percentages for the realization of hydrogen as an energy carrier. We are developing nonclassical polyhydride metal complexes as hydrogen storage materials. This class of materials can be tailored to reversibly release hydrogen at very favorable rates and temperatures both in solution and the solid state [1-4]. While attempting to develop complexes of improved available hydrogen densities, it was discovered that some polyhydride complexes act as catalysts for the low temperature, reversible dehydrogenation of cycloalkanes to aromatic hydrocarbons [5]. This catalytic system could be the basis for a low temperature, hydrogen storage system with a available hydrogen density greater than 7 weight percent.

We have found that iridium dihydrido complexes containing P-C-P pincer ligands are unusually robust and active catalysts for transfer dehydrogenation of cycloalkanes (cyclohexane, methylcyclohexane, decalin, and dicycolhexyl) to aromatic hydrocarbons (benzene, toluene, naphthalene, and biphenyl) [5]. For example, $IrH_4\{C_6H_3$-2,6-$(Bu^t_2PC_2H_4)_2\}$ (**1**) catalyzes the dehydrogenation of methylcyclohexane to methylcyclohexenes and toluene at rates of 186 and 94 turnover/h respectively at 200 °C. Appreciable activity was found at temperatures as low as 100 °C.

We have also found that **1** catalyzes the reverse reaction, the hydrogenation of arenes under 10 atm of hydrogen at 150 °C. The reactivity observed for the pincer

complex thus represents the basis for a hydrogen storage system with >7 weight percent available hydrogen content which operates under mild conditions. For example, we have found that **1** is a catalyst for the dicyclohexyl-biphenyl system seen in Scheme 1. This

Scheme 1
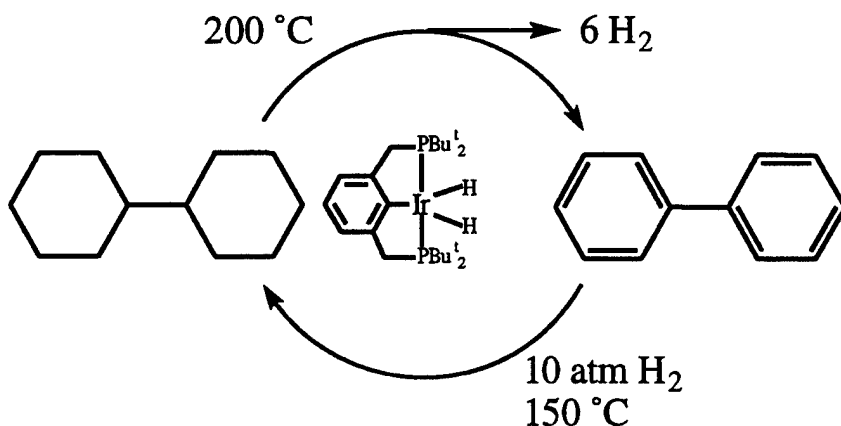
reactivity represents the basis for a hydrogen storage system with 7.2 weight percent available hydrogen content and which operates under mild conditions. This technology is epecially attractive since it is compatible with existing gasoline infrastructure. Finally, biphenyl has the advantage that, unlike toluene and naphthalene, there are no concerns about its toxicity and carcinogenicity.

A fundamental constraint of hydrogen storage systems based upon the reversible dehydrogenation of cycloalkanes to aromatic hydrocarbons is that equilibrium favors the aromatics only at temperatures above 200 °C. The P-C-P pincer complexes studied to date will activate cycloalkane C-H bonds and effect their conversion to aromatic hydrocarbons at temperatures as low as 100 °C. However, a hydrogen acceptor is thermodynamically required at the temperatures studied and free hydrogen was not produced in these systems. Above 200 °C the equilibrium favors of the production of hydrogen and the requirement of a hydrogen acceptor is eliminated. Unfortunately, the bis(phosphino)-m-xylenyl (type A) complexes which have been studied decompose at

these temperatures due to activation of the ligand methylene C-H bonds by the metal center. In order to circumvent this problem, we plan to synthesize related P-C-P 1,8-bis(phosphino)anthryl (type B) complexes. These complexes will have no C-H bonds
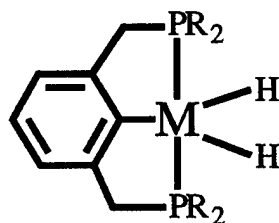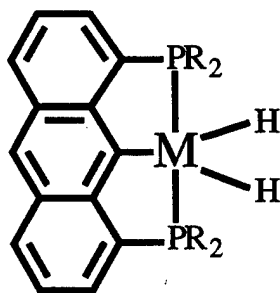
Type A   Type B

proximal to the metal center and should therefore have much greater stability than the xylenyl (type A) complexes. The related anthryl (type B) complex, PdCl{1,8-(Ph$_2$P)$_2$C$_{14}$H$_7$} has been previously prepared and found to be stable to its melting point of 300 °C [7]. It should be possible to prepare a wide variety of 1,8-bis(dialkylphosphino)anthracenes. This will allow us to vary the steric and electronic environments at the metal center and fine tune the activity of these complexes.

References.

1. Mediati, M., G.N. Tachibana, and C.M. Jensen 1990 *Inorg. Chem.* 29:3.

2. Mediati, M., G.N. Tachibana, and C.M. Jensen 1992 *Inorg. Chem.* 31:1827.

3. Le-Husebo, T., and C.M. Jensen 1993 *Inorg. Chem.* 31:3.

4. Lee. D.W., and C.M. Jensen 1996 *J. Am. Chem. Soc.* 118:8749.

5. Gupta, M., W.C. Kaska, R.C. Cramer, C.M. Jensen 1997 *J. Am. Chem. Soc.* 119:840.

6. Haenel, M.W., D. Jakubik, C. Kruger, P. Betz 1991 *Chem. Ber.* 124:333.

Hydrogen Storage via Reversible Cycloalkane Dehydrogenation Catalyzed by P-C-P Pincer Complexes

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Biphenyl/Dicyclohexyl
Pincer Complex
Hydrogen Storage System
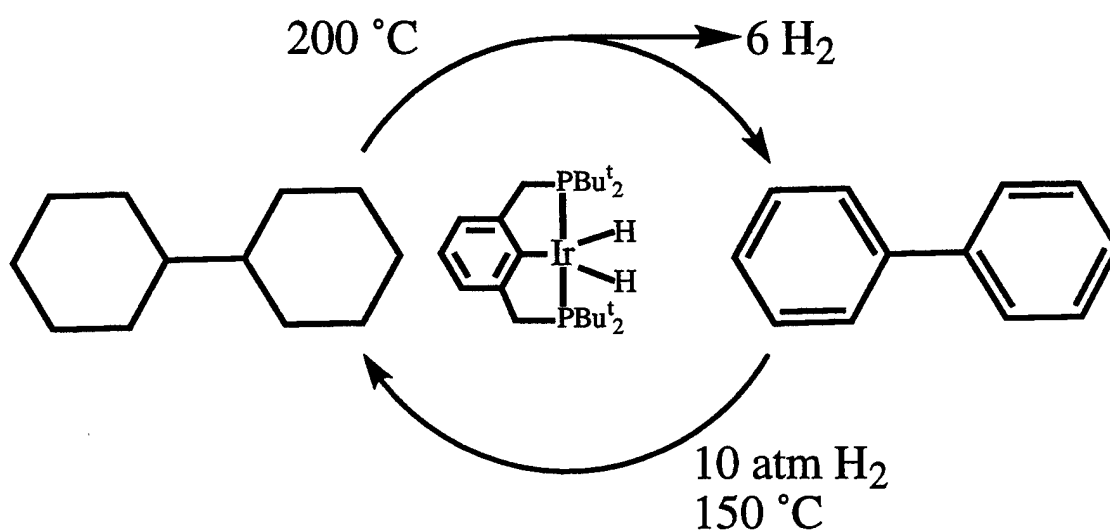
Advantages of Biphenyl-Dicyclohexyl Pincer Complex Hydrogen Storage System

- 7.2 weight percent available hydrogen.

- Dehydrogenation and hydrogenation at moderate temperatures.

- Highly robust catalyst.

- Homogeneous catalyst.

- Low toxicity and carcinogenicity.

- Compatible with existing infrastructure.

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Related Pincer Complex Catalyzed Reversible Dehydrogenations
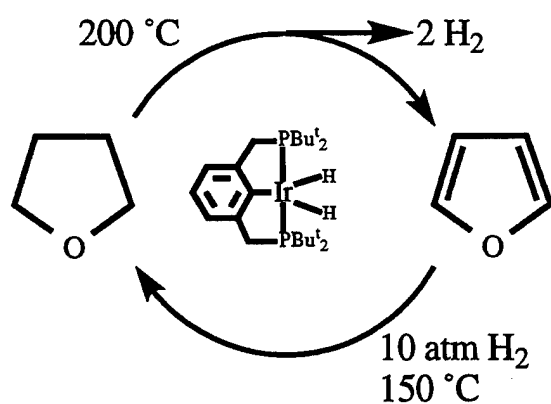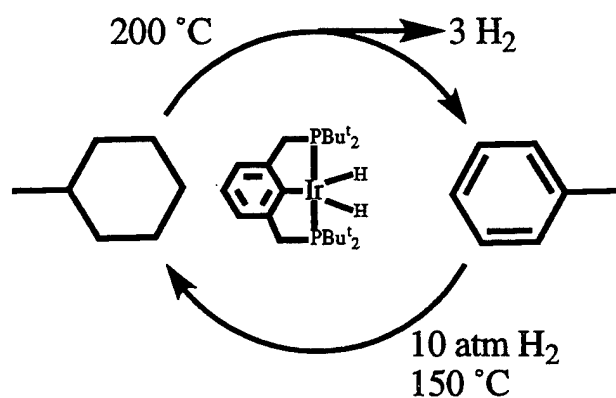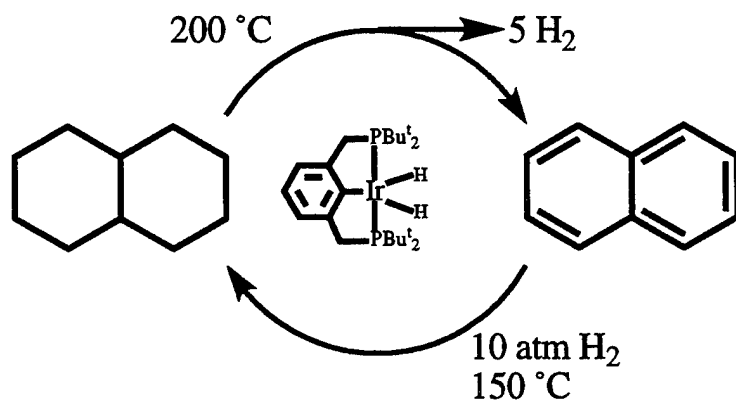
WORKING GROUP 3: Thermal and Catalyzed Processes

CATALYZED AND THERMAL PROCESSES

The participants in Session 3 were:

Frank Rose, Chair	Auburn University
Dave Bloomfield, Scribe	Analytic Power
Richard Bellows	Exxon
Jonathan Frost	Johnson Matthey Technology Center
Brian Wells	Ballard
Mohammed Entayetullah	H-Power
Richard Lawrance	Giner, Inc.
Jim Beckwith	Office of Research and Development
Kevin Drost	Pacific Northwest Laboratories
Robert Wegeng	Pacific Northwest Laboratories
Mark Cervi	Naval Surface Warfare Center
Bill Stinson	Kennedy Space Center
John Turner	National Renewable Energy Laboratory
Leslie Van Dine	International Fuel Cells
Peter Fedkiw	U.S. Army Research Office
Ed Starkovich	CECOM, U.S. Army
Peter Teagan	A.D. Little
Brian Barnett	A.D. Little
Chuck Call	Pacific Northwest Laboratories
James McElroy	Hamilton Standard

The Working Group on Catalyzed and Thermal Processes assessed seven different liquid or gaseous fuels which can be reprocessed to produce hydrogen. These fuels are ammonia, methanol, propane, methane, butane, gasoline and diesel fuel. Tables 1 and 2, found in the Executive Summary, summarize the material characteristics and weight and volume estimates. Tables 9 and 10 contain evaluations of the various systems and comparative aspects.

The session began with a presentation from the National Renewable Energy Laboratory on a solar electrolyzer with a projected efficiency of about 7 percent. The structure of the electrolyzer was analyzed in some detail and supporting experimental data from researchers in Hawaii were discussed. A second brief presentation was made by Analytic Power on the butane reformer technology available in Japan. The presentation was not in depth since there was little data on the Japanese device. The Japanese intend to go to the market in 2-3 years with a device in the 100-500 W range. The committee judged that the device would be somewhat comparable in size to the units discussed in detail in the workshop but would probably be less efficient.

The session participants spent some time clarifying the meaning of the terms in the four tables which were provided by the workshop organizers and filled out by the session participants. Since the focus of the session was to examine fuel reprocessing, potential fuels were listed and discussed in terms of their desirability for production of hydrogen. The most promi-

nent of the fuels were butane, propane, methanol, methane, gasoline, ammonia, JP-8 and diesel fuel. For processing, some of these fuels require the addition of water. In preparing the data, the mass of the water was included in the calculations of the weight and volume estimates presented in Table 2. The hydrocarbon and alcohol fuels listed in Table 1 are not all inclusive but consist of those fuels that were discussed within the context of the workshop. The tabular format for the data was modified somewhat by replacing the column "required ancillaries" with "comments."

The session participants examined ammonia, methanol, propane, methane, butane, gasoline, and diesel. Methane and ammonia possessed the highest specific energy of the fuels evaluated. With the exception of ammonia, all of the fuels considered within the workshop would have carbon monoxide in the hydrogen stream that must be reduced to tolerable levels prior to introduction to the fuel cell stack.

Table 2 shows the compilation of the participants' collective opinions of the mass of a system to required reform selected fuels as listed in Table 1. All of the units and processes surveyed appeared capable of scaling to small sizes although the confidence in scaling decreased as the size decreased. The data indicate that all of the units are within a factor of 2 in size and weight for the same performance. There is however a considerable difference in the complexity of the units. The ammonia processor and the mesoscopic fuel processor have the lowest weight and volume.

Table 9 is an evaluation of the resources needed and the time necessary to take each of the technologies discussed in the workshop to a demonstration phase. Several of the technologies are currently in development and will be demonstrated in less than one year. The mesoscopic processors are the least well developed and are roughly 2-3 years from laboratory demonstrations. In contrast, ammonia processors are contracted for delivery within one year. Successful demonstration of these fuel processors is estimated to be low risk for units to deliver more than 100 watts. For smaller units, such as the 10 W system specified in the tables, the risk is higher due to unknown scaling and to the ancillary equipment needed.

Table 10 is a compilation of the participants' estimates of the "state of the technology." Shelf life and stability under storage were not assessed to be an issue. Although there are sensitive catalysts in these systems, system purge before storage effectively eliminates this problem. The remainder of the systems are metallic or inert which means that properly stored, fuel processors have an "infinite" storage life. The areas where there were significant issues for all of the processors discussed were safety, environmental constraints, systems integration (especially in small sizes) and the manufacturing technology needed for mass production. In general, the uncertainty in the state of the technologies increased as the size of the units decreased. At the level of development for small fuel processors, cost is difficult to estimate. There was a consensus that on a "delivered energy basis" for the useful life of the processor, the cost of the unit would be small compared to batteries. There does not appear to be any insurmountable technological barriers to the development of small fuel processors that could function within the context of Army applications.

The session participants identified the following key issues that will directly determine the utility of small fuel processors. The most pressing are:

- Water recovery
- Impurity Management

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- Fuel

- Air

- Peripherals for units less than 50W

- Start up power

- Blowers

- Pumps

- Regulators

- Reliability of the peripherals

- Controls/sensors

- Systems Integration/Thermal Management

- Basic Flow Sheet

- Operating voltages for the peripherals

It was the unanimous opinion that some form of fuel processing would be used in the logistics for hydrogen fuel in the battlefield.

Table 9: Evaluation

Technology	Time to implementation Short=1-3 yrs Med=3-5 yrs Long=5+ yrs	Research/Resources needed	Probability of success for stated applications: Likely Possible Not Likely
Mesoscopic	2-3 lab DEMO	3-5 MM$ lab demo	Most components
	3-4 yr field demo	Field Demo Water recovery	Demo shift & pox not flow sheet risk @100 watts, peripherals problem
			Med risk
Hot Spot	1 year lab demo 1 year field demo	More rugged, Operating system, Flow sheet, Peripherals, 300K & 500K partner cost	Scaling to low power (10 watts) A moderate risk, 100-300 watts likely
Ammonia	Four months to field demo	500K	Minimal risk
Hybrid POX	Less than one year to Lab Demo, 1-2 year field Demo	1MM$	Cleanup risks common to hydrocarbons, low risk to 100 watts
Steam Ref	Japanese tech. Exists but at unknown level of performance		

Working Group: 3 **Chair: M. Frank Rose** **Scribe: Dave Bloomfield**

Table 10: Comparative Aspects

Rankings: 3=Significant issue; 2=Moderate issue; 1=Small issue; 0=Not Applicable

TECHNOLOGY	Mesoscopic	Hot Spot	Ammonia	Hybrid POX
1. Shelf life/stability under storage	1	1	1	0
2. Response time/load following	1	1	2	1
3. Flexibility in use (ease of stop/start; number of cycles; cycle speed)	1	1	1	1
4. Safety	2-3	2-3	2-3	2-3
5. Recharge time	0	0	0	0
6. Environmental restraints (operating T range; air quality required; orientation sensitivity; recyclable or disposable)	3	3	3	3
7. System integration constraints (Thermal match to fuel cell; water balance; parasitic power requirement)	3	3	3	3
8. Thermal signature	Not discriminator-operational constraint			
9. Manufacturability	2	2-3	3	1
10. Cost	All inexpensive to operate			

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SPE® HIGH PRESSURE HYDROGEN GENERATORS

FOR

TOMORROW'S HYDROGEN INFRASTRUCTURE

1997

J.F. McElroy

Hamilton Standard Division
United Technologies Corporation
Windsor Locks, Connecticut 06096

SPE CELL REACTIONS: WATER CYCLE

420
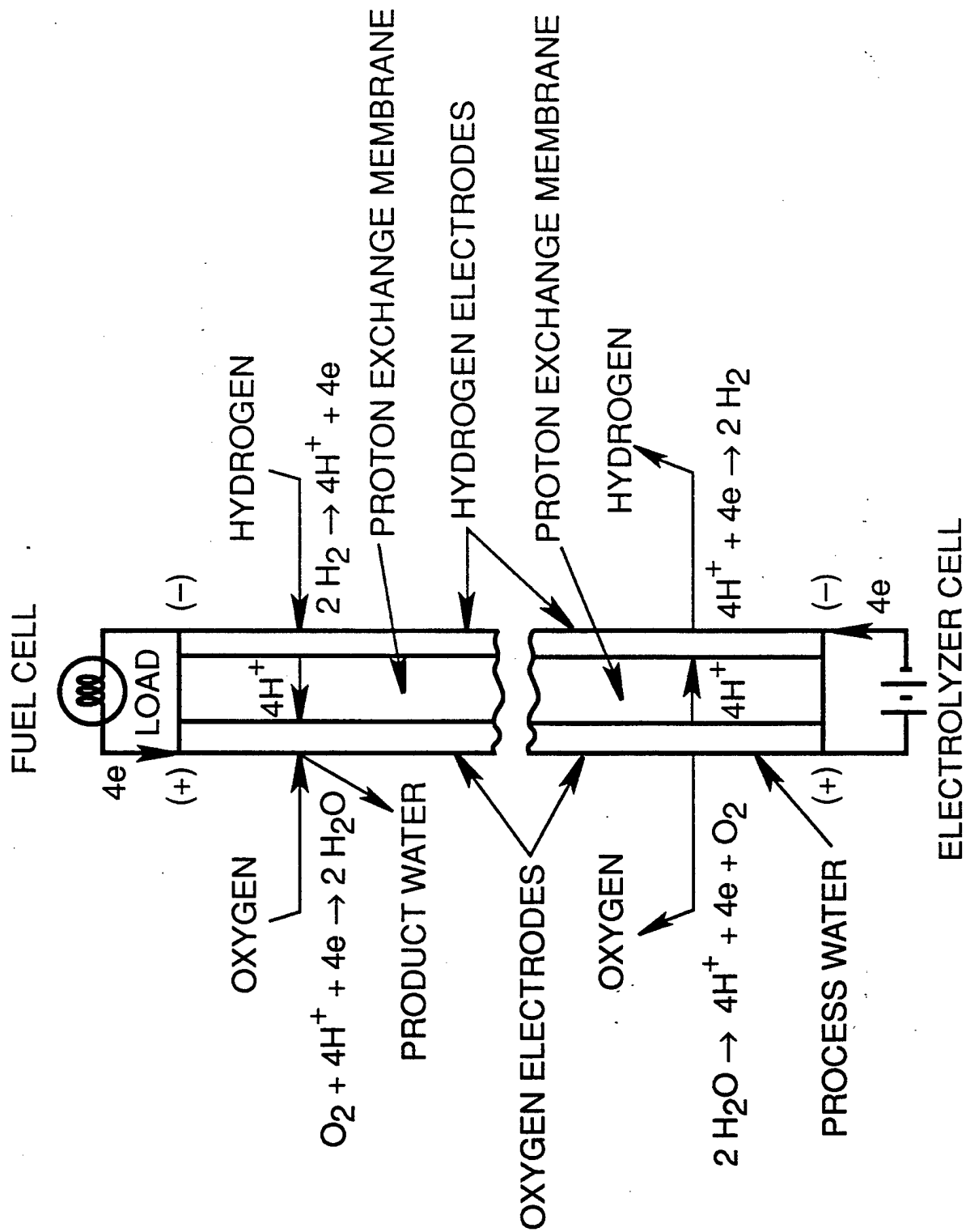
SUBMARINE LIFE SUPPORT SYSTEMS
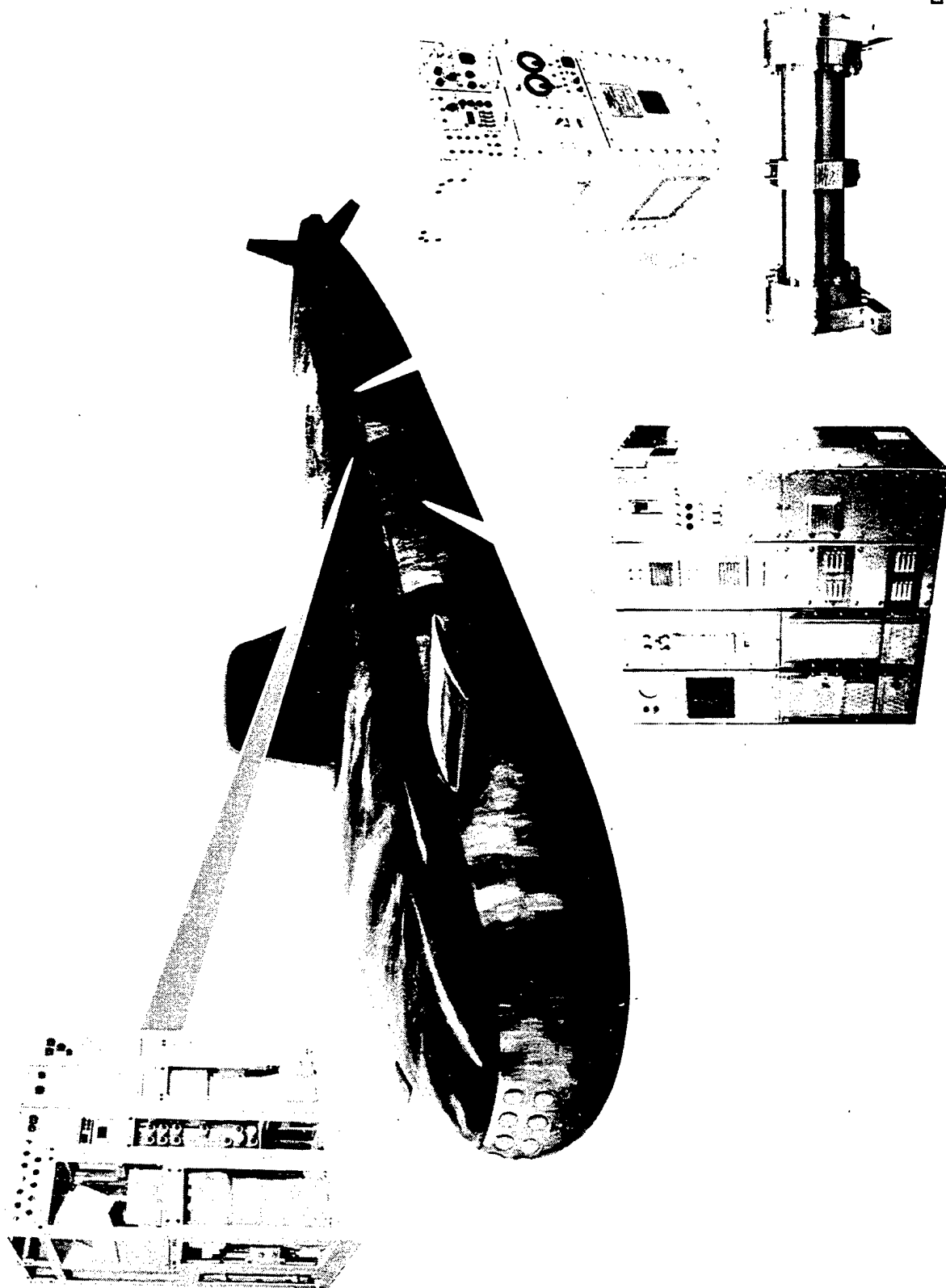
DG1636001

421

ON BOARD OXYGEN GENERATOR (2000 psi)

Power Supply

Pump

Sump

Cell Stack

H_2O Purity Sensor

H_2 Gas Detection Sensors

Relay Assembly

Filter

EG1077001ak-14

422
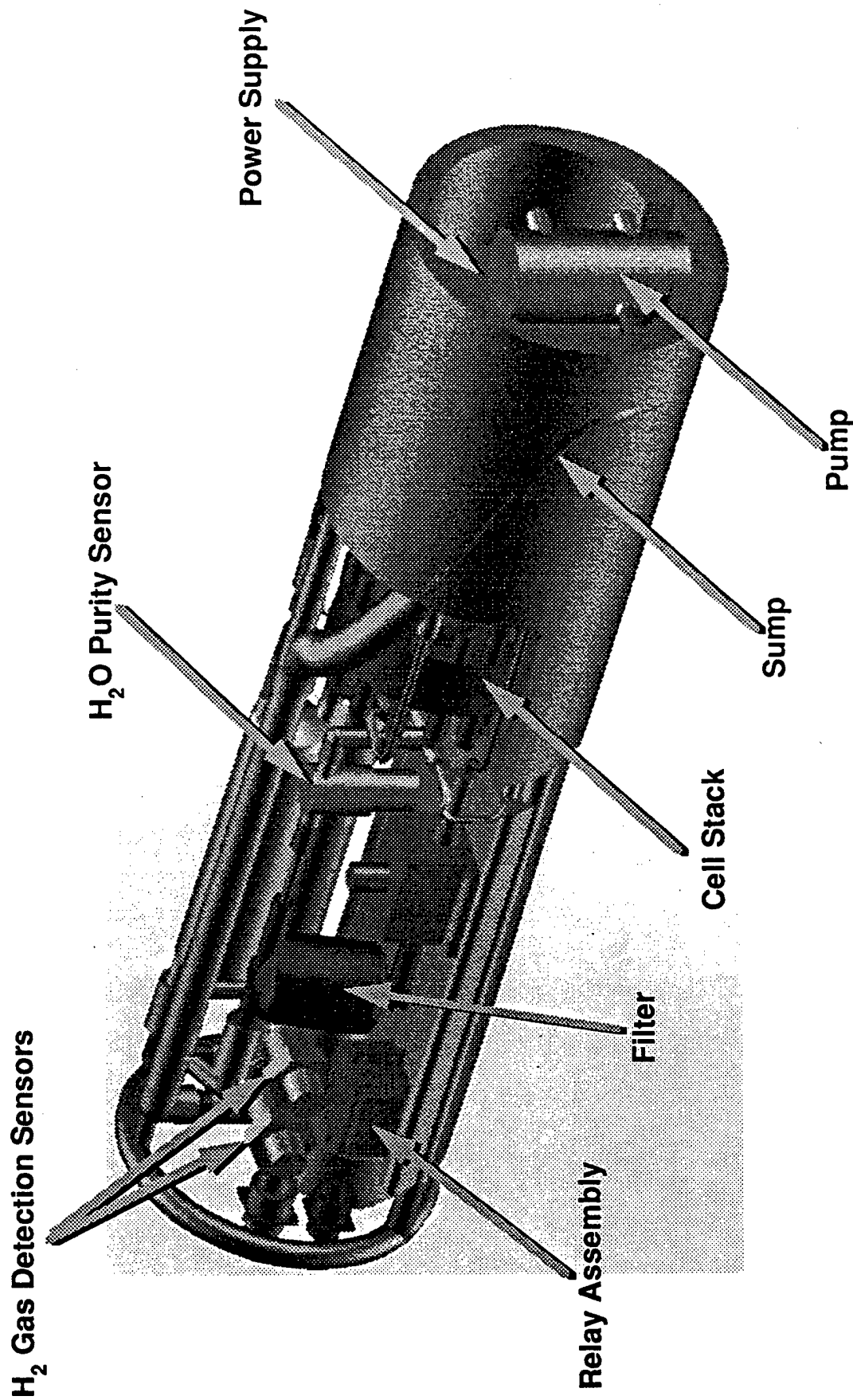
SPE HYDROGEN GENERATOR SYSTEM

Water Conditioner

Power Supply

O_2 Separator

H_2 Separator

Water Tank

H_2 Valves

Heat Exchanger

Water Pump

Cell Stack

EG107301ak-1

423
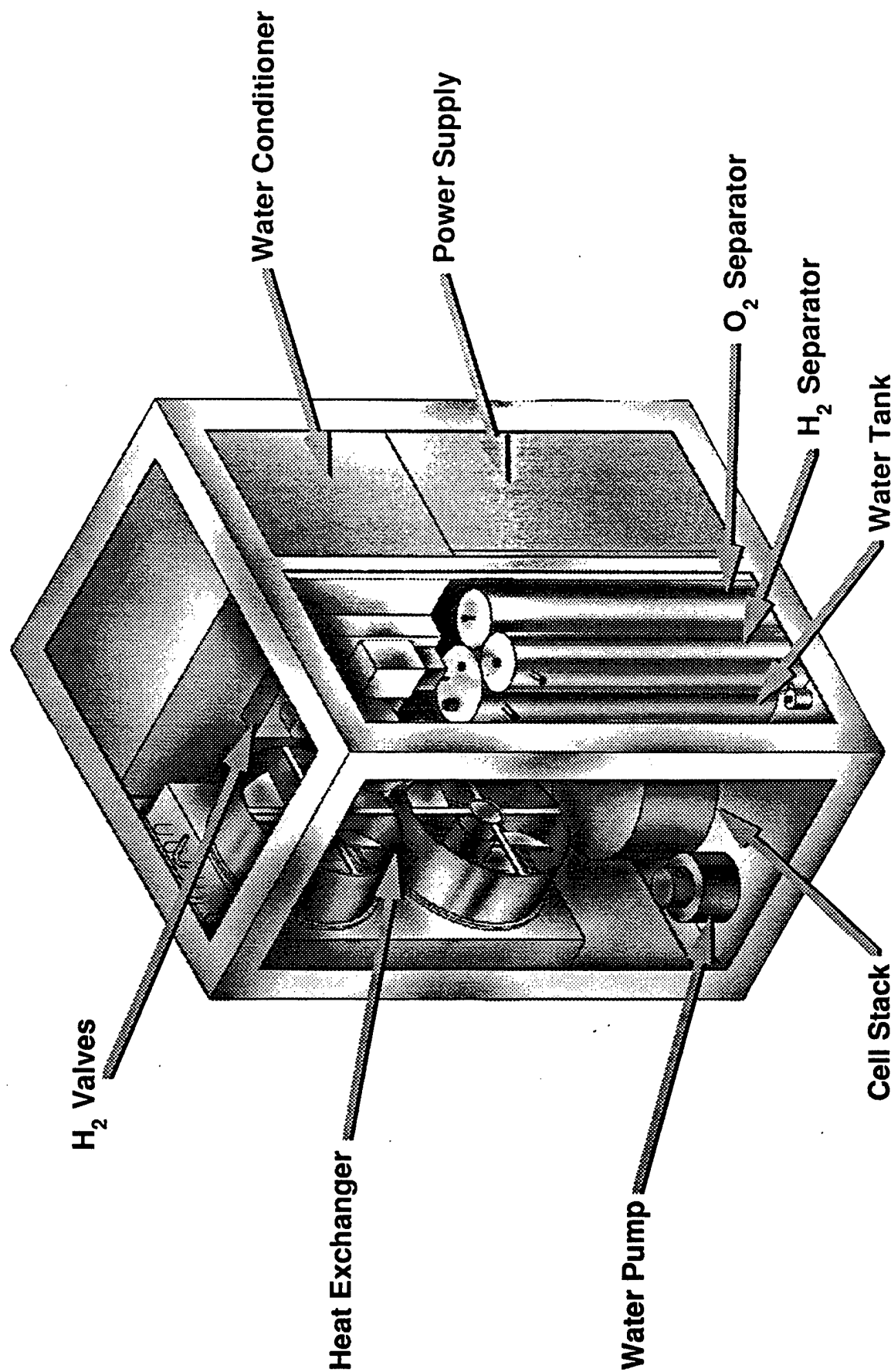
HYDROGEN FUEL GENERATOR FLUID SCHEMATIC WITH NEW CELL STRUCTURES

WATER PRE-TREATMENT

POTABLE WATER FEED

H_2O

HYDROGEN PRODUCT

P

H_2

H_2 PHASE SEP

LS

H_2 & H_2O

CELL STACK

(+)

(−)

H_2O

T W

RS H_2O

T

O_2 & H_2O

H_2O

LS

O_2

CG

O_2 SEPARATOR

H_2O RESERVOIR
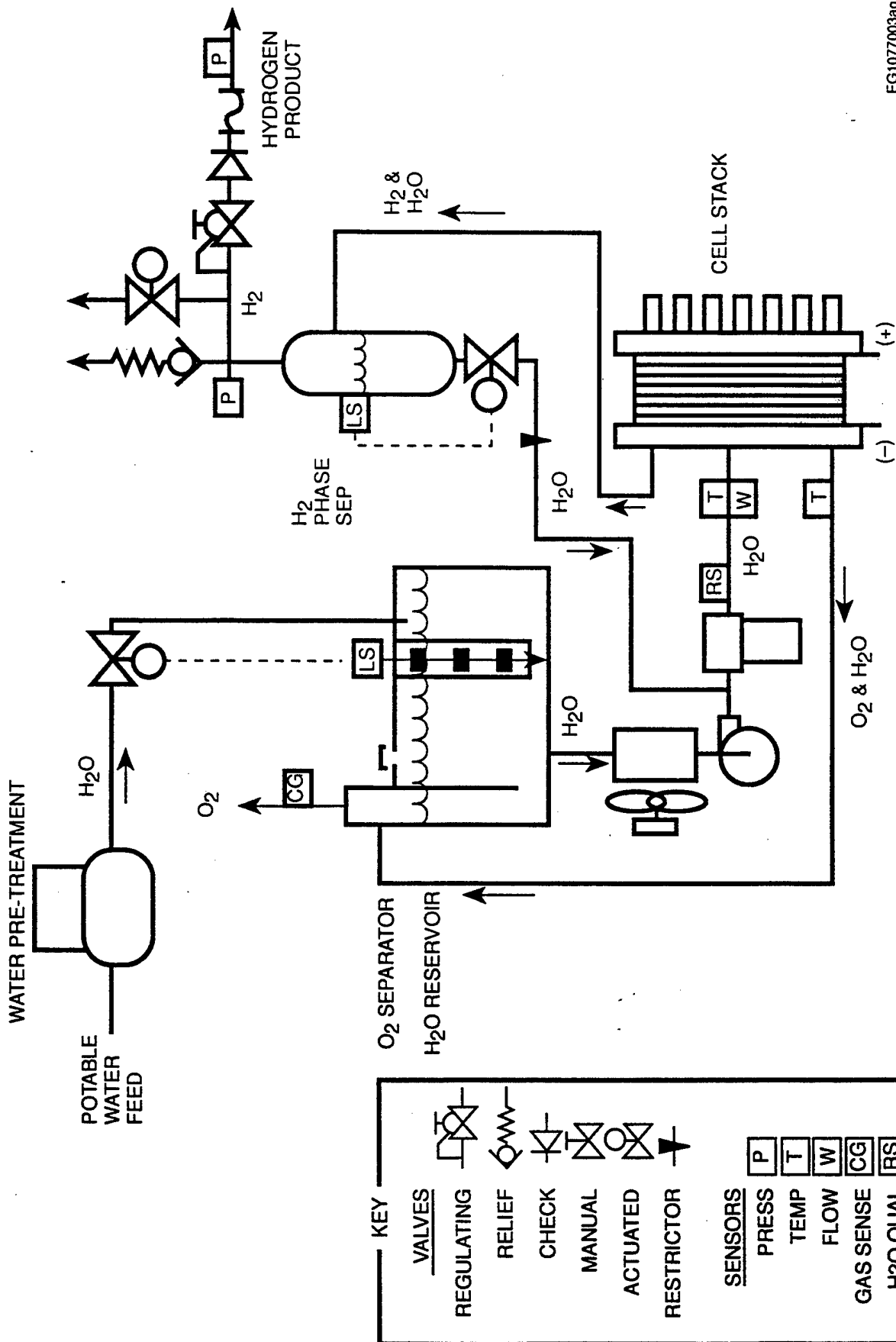
EG1077003ag

EG1077001ak-9

KEY

VALVES

REGULATING

RELIEF

CHECK

MANUAL

ACTUATED

RESTRICTOR

SENSORS

PRESS   P

TEMP   T

FLOW   W

GAS SENSE CG

H2O QUAL   RS

LEVEL SENSE LS

424

HIGH PRESSURE SPE GAS GENERATOR
(2000 TO 10,000 PSIG)
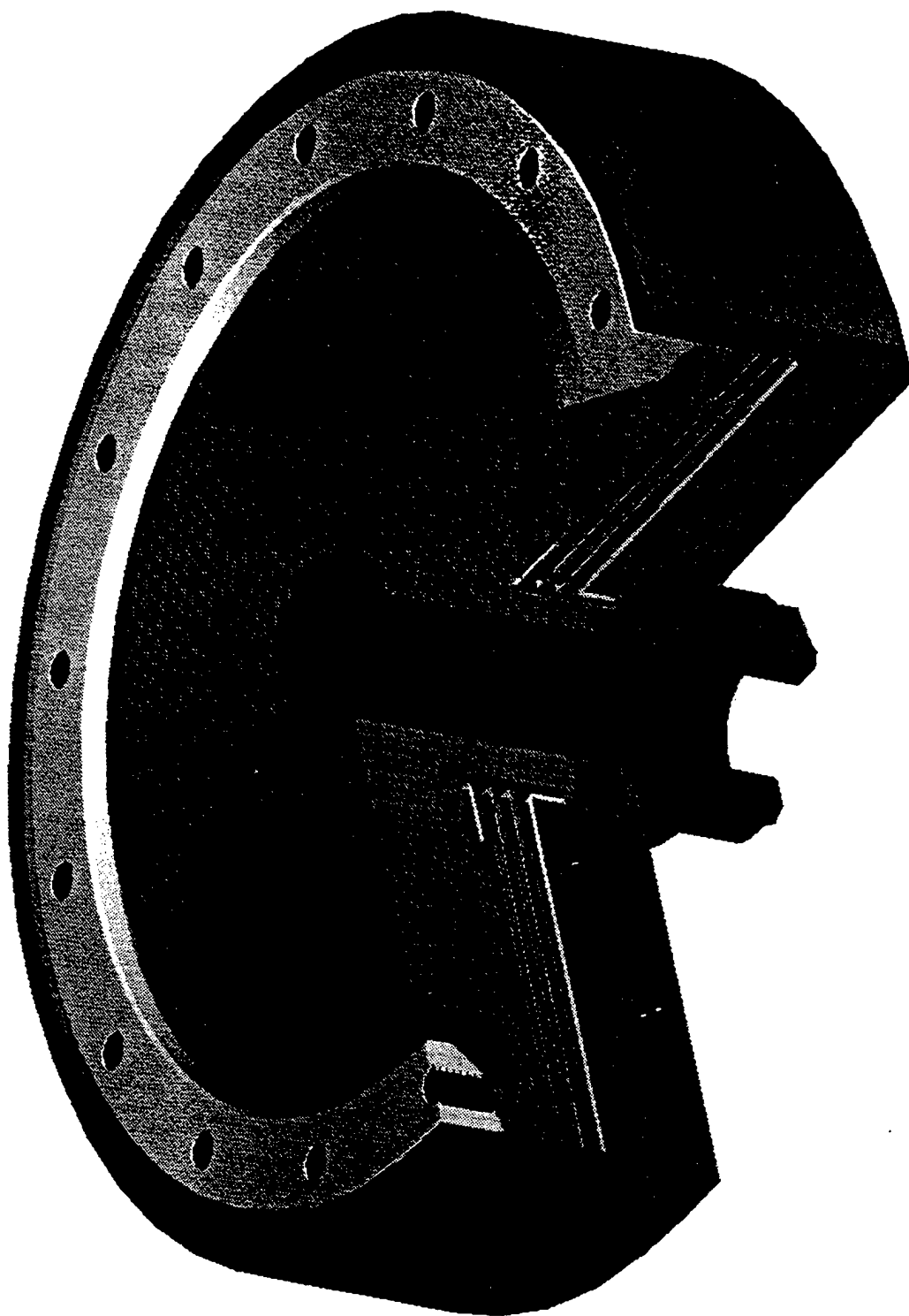
TYPICAL HYDROGEN GENERATOR STACK POLARIZATION CURVES

Cell potential (VDC)

Current density (ASF)

Metal laminate hardware

0.13 ft² active area

Nafion 117 membrane

2-cell stack; 120°F

○	Cell #1, 100 psig
◇	Cell #2, 100 psig
●	Cell #1, 750 psig
◆	Cell #2, 750 psig

EG107700¹ak-4

426
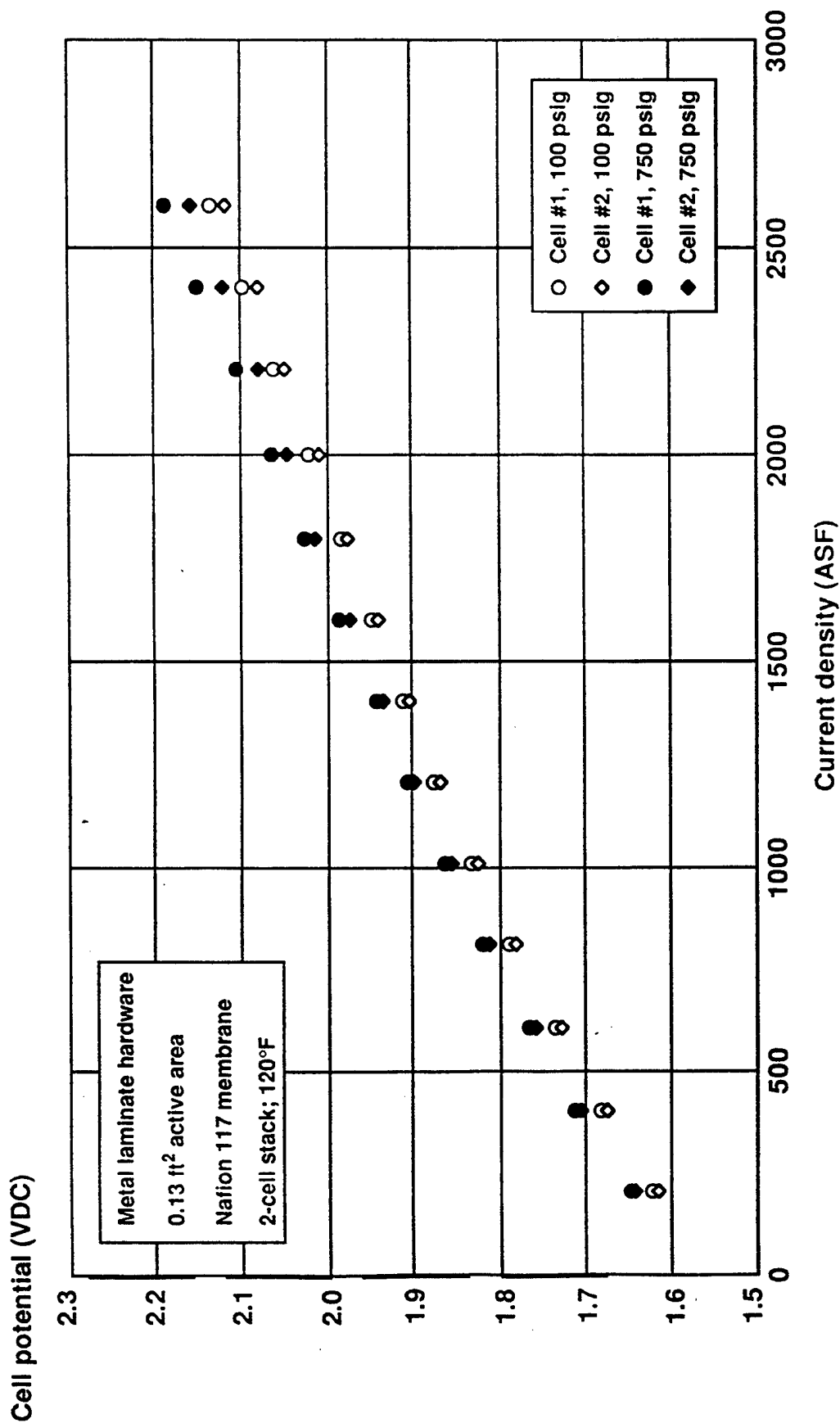
SUMMARY

- High differential pressure gas generators demonstrated (3000 psi proof - 2000 psi operating)

- Advanced design can be extended to 10,000 psi without exceeding membrane strength capabilities

- System hydrogen pressurization is electrochemically performed (i.e. no compressor nor high pressure water pump)

- High compression efficiency (i.e. >85% at 10,000 psig)

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April 8-10, 1997
Orlando, Florida

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7. APPENDICES

Appendix 1. Report by O. Velev

HYDROGEN STORAGE IN CHEMICAL HYDRIDES

Final Report

Contract No. 95F142000-000
TEES Project No. 47330

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HYDROGEN STORAGE IN CHEMICAL HYDRIDES
Executive Summary
Contract No. 95F142000*000

Broad Agency Announcement BAA 94-1 required the development of Small Power Sources with exacting specifications. The system proposed was a proton exchange membrane fuel cell (PEMFC) primary power source, operating on hydrogen. The hydrogen source may be refueled with hydrogen. The hydrogen could be stored as a rechargeable material (e.g., metal hydrides, fullerene hydrides) or in the form of expendable materials. The objective was a self-contained, maintenance-free power system delivering 430 kW over 180 days, with an hourly duty cycle of 300 W for 20 minutes, then 10 W for 40 minutes. The system goals were 1.2 kWh/liter and 650 Wh/kg, which were almost entirely determined by the reactants themselves.

At the time of proposed work, a PEMFC power source to meet the equivalent BAA 94-1 design goals was being developed by the Center for Electrochemical Systems and Hydrogen Research (CESHR), part of the Texas Engineering Experiment Station (TEES) in the Texas A&M University System (TAMU). About 3 kWh (10 hours) of baseline storage was required. The challenge was to attain the desired energy densities when storage sub-system parameters were included. To meet the goals of 1.2 kWh/liter and 650 Wh/kg, possible approaches were (a) Lightweight composite 300-500 atm (4,400-7,350 psi) pressure vessels for compressed gas storage; (b) Magnesium alloy and unconventional metal hydrides; (c) Fullerene hydrides; and (d) Chemical hydrides. The original proposal intended to examine all of the above, and select the most effective approach, but the objective of the referenced contract was to evaluate only (d).

To attain the goals via (d), only chemical hydrides producing hydrogen gas in contact with water are possible, since dissolving metals produce hydrogen from water in a 0.5 : 1 ratio. The most attractive of these are lithium hydride (LiH), lithium borohydride (sometimes called borohydrate, LiBH$_4$), lithium aluminum hydride (LiBH$_4$), and sodium borohydride (NaBH$_4$). LiH may effectively store twice as much hydrogen as a dissolving metal if LiOH is the reaction product: i.e., the hydrogen produced is equivalent to the water consumed, and the storage would be independent of an external water supply if 100% of the product water of the PEMFC could be recovered. In this case, LiH could store 25 wt % of hydrogen. If an anhydrous mixed oxide or salt is the product instead of a hydroxide, e.g., which may be the case with LiBH$_4$ under the correct reaction conditions, then the storage capacity would be 36.6% by weight of hydrogen. This would also make 100% water recovery unnecessary.

A literature survey showed that the composition of the products after reaction of hydrides with limited amounts of water was unknown in most cases. The concept depended on the appropriate combination of the highest possible water recovery from the PEMFC, combined with the least fixed water in the product. As a first step, water reactivity testing of selected hydrides was conducted in a Kipp generator as a function of temperature in the range -40°C and +65°C. Reaction rates and products were evaluated. The pure alkali and alkaline earth metal hydrides were stable to decomposition into their elements to temperatures exceeding 600°C (CaH$_2$, 600°C, NaH, 800°C, LiH, 800+°C). LiBH$_4$ was stable up to 275°C, but LiAlH$_4$ started to decompose at ca. 105°C, and its decomposition to LiH + Al + 3/2H$_2$ became rapid at 125°C. Since local temperatures in a Kipp-type reactor could easily exceed this temperature, LiAlH$_4$ was rejected as a candidate. The product of reaction between LiH and H$_2$O at reasonably low temperatures was not LiOH, but LiOH.H$_2$O. LiOH only formed at temperatures exceeding 125°C. Hence, a reactor designed to produce hydrogen from water in a 1 : 1 molecular ratio from LiH must operate at temperatures exceeding 125°C. If the water is solely derived from the PEMFC cathode effluent, 100% water recovery would be required. The reaction of LiH with pure water was rapid under all conditions, and the reaction generated a great deal of heat. This acted to seal off the surface of the reactant pellet with dry, solid reaction products when a reactor containing limited amounts of water was used. In a generator with intermittent water supply (e.g., a Kipp reactor whose water level varies with internal pressure, so that reaction only takes place as hydrogen is consumed and pressure falls) this meant that a time-delay effect occurred before further reaction took place. Similarly, when pressure increased, reaction continued to take place for some time after the solution level fell, since water was trapped within the porous LiH pellets. Excessive local heating was then difficult to control.

An atmospheric pressure Kipp generator must operate with a hydraulic seal of liquid water, protected from carbonatation (from air) via a low-density immiscible layer of e.g., silicone oil in contact with the atmosphere. Unless the generator is sealed and pressurized, it must operate below 100°C. Under these conditions, LiH only produces hydrogen from water molecule in a 0.5 : 1 ratio. This defeats the weight and volume objectives, since a

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large volume of excess water must be carried in the reactor. The major problem was undoubtedly the requirement for operation at a temperature higher than 125°C to achieve a 1 : 1 water : hydrogen stoichiometry with LiOH as the end product. This will either require a pressurized system operating on liquid water, or an innovative approach with water vapor as reactant.

In contrast to LiH, CaH_2 produces a pure hydroxide at low temperatures, therefore hydrogen from water at 1:1 stoichiometry. If the PEMFC unit cell voltage is 0.7 V, its storage capacity is 1.70 kWh/liter, 0.89 kWh/kg (LiH, 1.66 Wh/liter, 2.38 kWh/kg for LiOH product), which is within the specifications. If CaH_2 reacts at 580°C, it might produce two hydrogen molecules per water molecule recovered, since the end-product would be CaO. However, this is too close to its decomposition temperature and the reaction is not practical. MgH_2 (decomposition temperature, 280°C, 2.90 kWh/liter, 1.43 kWh/kg at 0.7 V) could also produce a hydroxide (but not oxide) end product, and has a lower equivalent weight. AlH_3 has an even lower equivalent weight (corresponding ca 3.9 kWh/liter, 1.88 kWh/kg), but its low decomposition temperature (100°C) makes its use impractical, if not dangerous. The only other compound of interest is $LiBH_4$ (two crystalline modifications, rhombic or orthorhombic, decomposition temperature ca. 275°, 1.25 kWh/liter, 1.90 Wh/kg, i.e., just within volume energy density specification). In the presence of limited amounts of water, it will react smoothly to hydrated lithium borate, $LiBO_2 \cdot 2H_2O$, i.e., $LiBH_4 + 4H_2O \rightarrow 4H_2 + LiOH.B(OH)_3$. However, its reaction rate with pure water or water vapor is extremely slow, due to the low intrinsic solubility of the lattice in water (the salt-like hydrides of the alkaline and alkaline earth metals are as intrinsically soluble as the corresponding chlorides). As a result, it must be used in an acidified environment to achieve reasonable reaction rates, e.g., in a Kipp-type generator containing sulfuric acid, which would not be within the energy density specifications.

The choice of material was narrowed to LiH (above 125°C), CaH_2, and MgH_2. The program undertaken included 5 W breadboard reactor design and construction. Its design depended on the results of reaction rate modeling conducted. A pressurized sealed Kipp reactor is in principle possible for LiH above 125°C. For safety reasons, it would require an active mechanical pressure control to 2.0-3.0 atm (gauge). This was not considered, because the rapidity of the reaction, and the time delays discussed above. The accompanying local heat production made the system impractical to control, although thermal runaway is improbable. Even if it may be technically feasible, this reactor was not considered because it needs a large passive reservoir of water for thermal control. A properly designed system could be passive and require no particular attention, but it would not meet energy density goals. A system using an Archimedian-screw hydride feed to the reactor was constructed, but its reliability was dubious.

In all cases, the requirement for water recovery from the fuel cell was a major problem. Simple condensation recovery schemes could not meet the goal. The only possibility appeared to be a scheme using the chemical desiccant properties of the hydride itself. The design of a reactor using a membrane dehumidifier operating with cathode effluent on one side and metal hydride (CaH_2, MgH_2) on the other is presented. Water is very soluble in the membrane (ion-exchanged Nafion™ perfluorocarbon sulfonate, Du Pont de Nemours), whereas hydrogen is not. This may be used to recover hydrogen for the PEMFC. Such a design may work, but the 100% recovery requirement is still difficult to satisfy. It was decided that work would be better terminated, rather than attempt to build such a system. One problem, which was not considered, is that of possible contamination of the PEMFC electrolyte by alkaline carry-over, although this should be minimal with CaH_2 or MgH_2 as reactants.

While the inevitable conclusion was that a PEMFC system with close to 100% water recovery using CaH_2 or MgH_2 for hydrogen storage in a foolproof system would be a very difficult, if not impossible, proposition, another much more workable solution was given in the original proposal. If the fuel cell is alkaline (with a chemical CO_2 scrubber on the air side), the reactant water is formed in the anode stream, which may be directly circulated over CaH_2 or MgH_2 in a hydrogen feedback loop. This will avoid the problem of product water separation, and permit the program goals to be achieved. Work on this solution is recommended in future, if the need for this power source still exists.

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HYDROGEN STORAGE IN CHEMICAL HYDRIDES

1. Proposal and Anticipated Difficulties

1.1. Introduction

The referenced contract was awarded after the contractor responded to Broad Agency Proposer Information Pamphlet BAA 94-1. This required the development of Small Power Sources with the specifications: Energy Density: > 650 Wh/kg, > 1200 Wh/liter; Discharge Time: Minutes to several hours; Discharge Rates: High values for pulsed loads, with power densities in the same range as those of Ni/Cd or Pb/acid batteries, i.e., 150 W/kg; Lifetime: Shelf plus operational life up to several years without loss of performance; Energy Production: Preferably no expendable materials for energy production - preferably extract energy from some characteristics of the environment at rates and efficiencies higher than state-of-the-art.

These characteristics represented a combination of properties required for both Primary and Secondary Power Sources. The system proposed was a proton exchange membrane fuel cell (PEMFC) primary power source, which would be fueled by hydrogen, and which may be refueled (depending on needs) with hydrogen produced from either electricity and water from the environment in an electrolyzer similar in principle to the PEMFC, or by the use of expendable materials.

A proposed PEMFC power source design to meet these goals was based on previous studies by the Center for Electrochemical Systems and Hydrogen Research (CESHR), part of the Texas Engineering Experiment Station (TEES) in the Texas A&M University System (TAMU), with some supporting research by Los Alamos National Laboratory (LANL), and by MER Corporation (Tucson, AZ). MER is a small business specializing in advanced materials, including metal-non-metal composites, and fullerenes.

A 6 V (minimum), ca. 8 V (maximum) PEMFC multicell stack was proposed to minimize the weight and volume of both the power source and auxiliaries. The desired BAA voltage requirements (12 and 24 V) could be met by use of dc-dc converters. The stack would contain 10 cells with 100 cm^2 electrode active area. This cell size is scaled to a postulated maximum gross power requirement of 360 W, which assumes operation at a conservative current density of 600 mA/cm^2 at 0.6 V on stored hydrogen and ambient air at atmospheric pressure, a performance then routinely obtainable at CESHR. The power output could be scaled as desired by changes in cell area and in the number of cells in the stack. Corresponding changes in terminal stack voltage would be accommodated by the dc-dc converter. The design of the lightweight PEMFC stack was based on an ultra-light air-cooled atmospheric pressure design proposed in April 1994 to ARPA by CESHR/TEES in response to BAA 94-427, which was awarded in 1995. For simplicity and because of the requirement for zero maintenance, it would use internal self-humidification by product water, now a proven technology. No lifetime problems were anticipated with the PEMFC sub-system, which has demonstrated 40,000+ hour lifetimes with 20 year old components.

About 3 kWh (10 hours) of baseline storage was proposed. Hydrogen is the ideal reactive fuel for PEMFCs. Its lower-heating-value of combustion (33.4 kWh/kg) yields a practical 13.3 kWh/kg in a fuel cell operating at 0.6 V with 17% total losses for parasitic power (cooling,

electronics). The challenge was attaining the desired energy densities when storage sub-system parameters are included. To meet the BAA 94-1 goals of 1.2 kWh/liter and 650 Wh/kg, the following approaches were selected:

- Lightweight composite materials for cylinders for gas-phase storage at pressures as high as 300-500 atm (4,400-7,350 psi);
- Metallic hydrides based on magnesium alloys (Mg_2Ni and unconventional systems) and on metastable alloys of Ti-Al type to increase energy density compared to conventional metal hydrides;
- Hydrogen on fullerenes, which may show at least 1 reversible H per 1.7 C;
- Chemical hydrogen storage, including metals, alkali metal hydrides;
- The use of hydrazine in aqueous solution as an alternative PEMFC fuel to hydrogen. The danger in this case was the possible formation of hydrazine salts of the sulfonic acid groups of PEM materials.

All of the above were proposed for comparative assessment under the program.

Two possible approaches exist, namely dissolving metals and chemical hydrides. The former include Fe, Zn, Al and Mg, and may also include Li. Studies at H-Power, Inc. (Bloomfield, NJ) have shown that a sponge iron/water system could store as much as 3.6 wt. % (including the system weight) and efforts are on the way to build a demonstration prototype/vehicle. Aluminum, on the other hand, may be able to "store" about 5.5% by weight of hydrogen. Another possible storage material is an ionic hydride. These produce hydrogen gas in contact with water, giving an alkaline reaction product for metals with soluble hydroxides. The most attractive of these compounds appeared to be lithium hydride (LiH), lithium borohydride (sometimes called borohydrate, $LiBH_4$), lithium aluminum hydride ($LiBH_4$), and sodium borohydride ($NaBH_4$). LiH effectively stores twice as much hydrogen as a dissolving metal provided that LiOH is the reaction product: i.e., the hydrogen produced is equivalent to the water consumed. If a mixed oxide or salt is the product instead of a hydroxide, e.g., which may be the case with $LiBH_4$ under the correct reaction conditions, the hydrogen produced is twice as much as the equivalents of water consumed. This is clearly advantageous, since it makes 100% water recovery unnecessary. Thus, LiH can in principle "store" 25 wt. % of hydrogen and $LiBH_4$ can correspondingly "store" 36.6 wt. %. In contrast, metallic Li stored only 14.4 wt % of hydrogen. The whole of this storage capacity per unit weight may be used, provided that 100% and 50% of the PEMFC product water can be recovered. It was felt that not all of this product water could in fact be recovered. In consequence, a mixture of these hydrides in a reactor of special design was proposed, which would incorporate a membrane humidifier (spent air drier). The development of such a reactor was proposed. Even including the reactor, the energy densities per kg and per liter would largely exceed the BAA specification requirements.

1.2. Work Initially Proposed

High-risk/high-payoff Task Areas were identified as those involving hydrogen storage and hydrogen supply to the fuel cell. If the weight content of hydrogen in the storage or generation sub-system exceeded 5%, the energy density goals of BAA 94-1 could be met.

The proposal was for a three-year, $2.01 million contract, which would deliver a 300 W Small Proton Exchange Fuel Cell Power Source with one selected breadboard hydrogen storage

system of 3 kWh capacity, Power Electronics, and Pulse Power Battery or Electrochemical Capacitor Subsystems. The Power System will be designed for 300 W nominal output, energy storage up to 3 kWh, with any required pulse power from a Ni/Cd or Pb-acid battery.

Project success was considered to depend on: (1) the development of lightweight bipolar plates and endplates in bonded PEMFC stacks, to reduce weight as far as possible; and (2) significant enhancement of the energy densities and specific energies for hydrogen storage generation. For the latter, it was proposed that subcontractors LANL and MER would examine advanced materials for the high pressure gas phase storage of hydrogen. New hydriding alloys based on magnesium Mg and on metastable Ti-Al materials were proposed, in partnership with LANL, which might allow much higher weight percent hydrogen storage than state-of-technology materials (up to 4.8 wt %, compared with up to 1.5 wt %). MER would also examine the absorption of hydrogen on fullerenes, since there is some evidence that semi-reversible absorption takes place up to the composition $C_{60}H_{36}$, which would allow up to 4.75 wt % hydrogen storage, excluding containment.

A detailed Statement of Work was provided, divided into three Tasks. Task 1 and its associated Subtasks included the development of 100 cm^2 active area PEMFC membrane-electrode assemblies (MEAs) which could operate in the temperature range 30°-70°C at 0.6 V and 600 mA/cm^2 (at 50°-60° C) with air at atmospheric pressure, under conditions of internal self-humidification using product water, the incorporation of such MEAs into lightweight bipolar hardware, and assembly and testing of 10-cell fuel cell stacks after appropriate thermal management modeling and experimental analysis.

Task 2 would have compared different methods of hydrogen storage, namely as a compressed gas in tanks made from lightweight composite materials, including high-strength graphite fibers, as metal hydrides in novel lightweight metastable hydriding alloys, as fullerene hydrides, as hydrazine, and as chemical compounds producing hydrogen on reaction with water. One of these storage methods was to be selected for combination with the PEMFC DC power module. Task 3 was to study auxiliaries and electrical system considerations, such as power electronics, batteries and/or electrochemical capacitors for peak power applications, and systems integration and testing. This would result in production of the deliverable device discussed above.

1.3. Chemical Hydride Reactor Development

The part of the Subtask dedicated to the chemical hydride reactor (Subtask 2.4) would have selected hydride compounds from among the class represented by LiH, LiAlH$_4$, LiBH$_4$ and NaBH$_4$. The reactivity of these materials would be examined in the "as received" condition and after encapsulation with a porous organic coating dissolved in a suitable solvent, e.g., of materials such as polyamides dissolved in acetone or diethyl ether. Reactivity testing would be first conducted as a function of ambient temperature in a standard Kipp generator constructed of chemical glassware, which is traditionally used in analytical chemistry laboratories for the "as-required" production of, e.g., hydrogen sulfide (H$_2$S) from insoluble inorganic sulfides and dilute sulfuric acid (H$_2$SO$_4$) or hydrogen from zinc or magnesium turnings and H$_2$SO$_4$. A traditional Kipp hydrogen generator is shown in Figure 1.

Emphasis was to be on the feasibility of operating this type of reactor at all ambient temperatures in the range −40°C and +65°C. Following the choice of suitable hydrides and/or mixtures, subscale generators incorporating wicking arrangements for operation under all orientations shall be constructed and tested. The water make-up source for the PEMFC

generator shall be either an air-cooled condenser, fed by humidified air saturated with water vapor at 65°C simulating PEMFC cathode exit conditions, or more favorably a membrane drier/humidifier incorporating an area of Nafion® or other suitable membrane through which rapid water diffusion occurs. Upon satisfactory demonstration of the performance of model generators subscale boiler-plate PEMFC fuel cells would be tested together with the generators in integrated units.
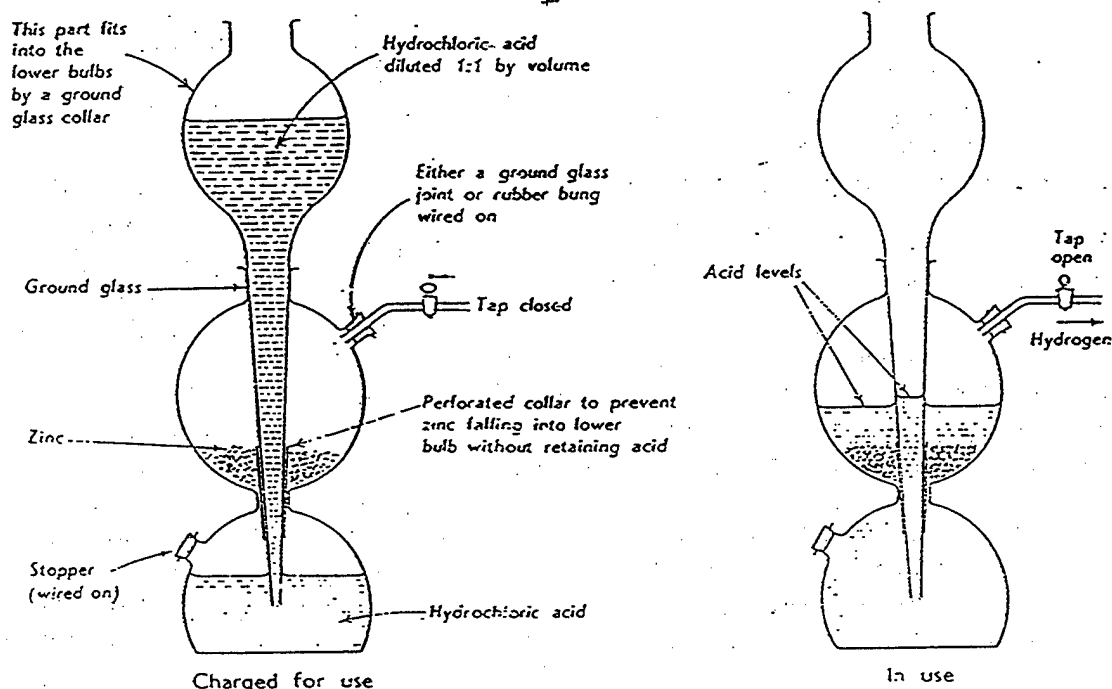
Figure 1. Traditional Kipp Hydrogen Generator.

1.4. Potential Problems With Chemical Hydrogen Generators

1.4.1. General Problems

For the chemical hydrides, success depended on the development of a suitable reactor with effective product water recovery from the fuel cell and effective water management. It also depended on the formation of the correct type of reaction products. It was originally felt that any form of mechanical feed of hydride reactant would be impractical, since it would be unreliable and would require electric drive mechanisms. Such a system would be only examined as a last resort. A major unknown which could throw doubt on the project as a whole was the effect of blockage of the active part of the reacting system by previously formed reaction products. Even the precise nature of the products was unknown in most cases, e.g., for LiBH4. The literature would only report on the product formed in a large excess of water: in this case, it

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would be the slightly soluble metaborate, $LiBO_2$, undoubtedly in a hydrated form. However, for this proposal, stoichiometric amounts of water would be reacted with the material, which should result in solid dehydrated metaborate. No previous published experience existed on the kinetics of this process, and indeed on whether a solid metaborate layer would not seal off the surface of unreacted $LiBH_4$, effectively passivating it and preventing further reaction.

1.4.2. Reactor Designs

The most obvious generator design for a dissolving hydride reactant would be of the Kipp variety, as originally proposed. A Kipp generator would contain an initial excess of water as reactant, with hydrogen produced by previous reaction under slight pressure. The pressure differential between the inside of the hydrogen-filled reactor and atmospheric pressure outside would lower the volume of the water inside, since the water would be in a container of U-tube type in barometric equilibrium with the atmosphere. Thus, the reaction would stop when the water level fell below the hydride reactant container inside, where any remaining water reacts until the system is locally dry. This may be accompanied by local heat production, which may cause some spot-heating. This was a further problem to be addressed. The excess hydrogen pressure is only a few inches of water, which is consistent with safety considerations. The reaction stops until the excess hydrogen is used by the fuel cell, when the pressure will fall to approach atmospheric, and more water then enters the reactant container. The hydrogen produced is prehumidified, which would help the fuel cell to attain maximum performance.

The simple Kipp generator must be initially charged with an excess of water to create the barometric column. However, water is consumed by the reaction as hydrogen is produced. This water would be supplied by make-up water as required from a condenser/dehumidifier operating from the fuel cell cathode exit air flow. The presence of excess water will tend to mitigate the effects of reactant passivation discussed above, however the presence of passivation films on the hydride reactant when the water reactant became saturated with reaction product was remained a further unknown.

1.4.3. Orientation and Portability

The simple Kipp generator relies on gravity for reactant switch-off under pressure. Even the design and practical operation of such a device would not be a trivial undertaking. If portable applications were required, the operation of the generator should remain independent of orientation. In consequence, an orientation-independent version of a Kipp generator would then be required. One approach would contain a flexible capillary sponge or wick which could be active in all orientations. If the sponge structure is more open towards the outside of the diameter, excess water will accumulate at the bottom of the system when the pressure rises and the hydrogen evolution reaction stops or slows down.

1.4.4. Interfacing Chemical Hydrides to the PEMFC

The water reactant, i.e., the product of the PEMFC cathode reaction, brings with it dissolved nitrogen with some oxygen from the cathode air supply, which can accumulate in the system as hydrogen is consumed. Therefore a small bleed of reactant via a permeation tube is required from the cathode. Such a generator is relatively simple to construct and is safe to operate if it is used for a stationary application since it could in principle assure fail-safe operation. Its

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operation is fully automatic, and no special safety precautions are needed, provided that the container remains sealed.

1.4.5. Possible Neutralization of PEM Material

One further potential major problem with an alkali-metal hydrogen generator coupled to a PEMFC is that alkaline products may react with the acid membrane, causing neutralization. If LiBH$_4$ is used, hydroxides will not be the product. However, a porous Teflon® filter between the generator and the fuel cell will assist in protecting the PEM by preventing aerosols from passing over.

2. Conclusions - The Hydride Reactor

Even though the hydride reactor looked attractive on paper because of its potentially high weight percent of hydrogen storage (again on paper), we most certainly considered it to be high-risk compared with the alternative approaches, i.e., hydrogen storage at high pressures and/or in special hydriding alloys, or on fullerenes if this approach should have proved to be kinetically feasible.

The reactive chemical hydride was considered to be high-risk R&D, since a reactor based on stoichiometric reaction with fuel cell product water to produce exactly the required amount of hydrogen to feed the fuel cell (i.e., corresponding to the differential current requirement) may never work at all.

3. Summary of Contract Number 95F142000-000

3.1. Objectives

The objectives of the project were to use available or experimentally measured thermodynamic and kinetic data to select and evaluate lightweight (i.e., low equivalent weight) hydrides producing hydrogen from water in a prototype reactor, and design a reactor for controlled generation of hydrogen for use in a PEMFC. The design goal was the development of a self-contained feed-back hydrogen-generator PEMFC power system capable of delivering 430 kW over 180 days, with an hourly duty cycle of 300 W for 20 minutes, then 10 W for 40 minutes.

3.2. Task 1.2. Literature Survey

3.2.1. Subtask 1.2.1. Chemistry of Hydrogen Generation by Hydride Reaction with

Water

Possible low-equivalent-weight hydride reactants are LiH, LiBH$_4$, LiAlH$_4$, NaBH$_4$, together with calcium hydride (CaH$_2$). All these materials are salt-like, and contain H$^-$, BH$_4^-$, and AlH$_4^-$ anions. Stability considerations are a concern with certain complex low-equivalent-

weight hydride compounds. While $LiBH_4$ is stable up to 275°C in the absence of air, under the same conditions $LiAlH_4$ starts to show signs of decomposition at about 105°C, and decomposition becomes rapid at 125°C (Reaction 5, below). Calcium hydride decomposes into its elements at about 600°C, and sodium hydride at about 800°C. Lithium hydride is more stable than these. Hydrogen-producing reactions occurring with these compounds are as follows:

$$LiH + 2H_2O \rightarrow H_2 + LiOH.H_2O \ (T < 125°C) \tag{1}$$

$$LiH + H_2O \rightarrow H_2 + LiOH \ (T > 125°C) \tag{2}$$

$$LiBH_4 + 4H_2O \rightarrow 4H_2 + LiOH.B(OH)_3 \tag{3}$$

$$LiAlH_4 + 4H_2O \rightarrow 4H_2 + LiOH.Al(OH)_3 \tag{4}$$

$$LiAlH_4 \rightarrow 3/2H_2 + Al + LiH \tag{5}$$

$$Al + LiOH + H_2O \rightarrow 3/2H_2 + LiAlO_2 \tag{6}$$

$$NaBH_4 + 4H_2O \rightarrow 4H_2 + NaOH.B(OH)_3 \tag{7}$$

$$CaH_2 + 2H_2O \rightarrow 2H_2 + Ca(OH)_2 \tag{8}$$
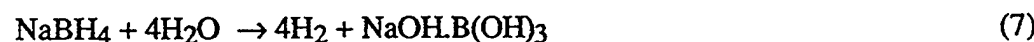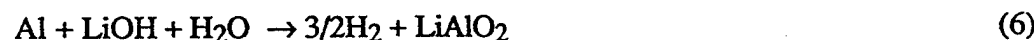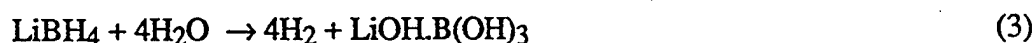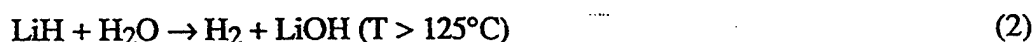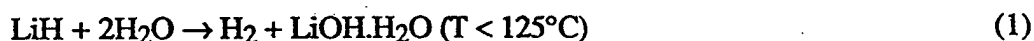
We should note that the amount of hydrogen available from the compounds depends on the reaction products formed. In some cases, the product of reaction may form a film over the hydride reactant. If this film is impervious to water, the reaction may not go to completion. For example, the reaction product in Equation 3 has these characteristics if pure water is used as the reactant, since the mixed hydroxy-compound (or hydrated borate salt) is rather insoluble at alkaline pH associated with the reaction product. If the material is acidified, the reaction proceeds smoothly. However, this implies the supply of an acid and excess water.

To use another example, the remaining water in $LiOH.H_2O$ does not appear to react further with LiH (or indeed with lithium metal) until the temperature exceeds 125°C to complete Reaction 2. Reactions 3 and 4 are analogs of Reaction 2, since the reaction products contain no bound water as such. In principle, if the reaction temperatures are sufficiently high, LiH (or Li metal) will react with the water present as hydroxide in the reaction product, giving oxides or anhydrous oxide compounds. For example, the mixed hydroxide product of Reaction 3 could in theory decompose to $LiBO_2$, releasing two further molecules of water, which could react with another $LiBH_4$ molecule to give four more H_2 molecules. Thus, at a sufficiently high temperature,

$$LiBH_4 + 2H_2O \rightarrow 4H_2 + LiBO_2 \tag{9}$$

The same type of process occurs in Reaction 4 followed by Reaction 5, giving overall:

$$LiAlH_4 + 2H_2O \rightarrow 4H_2 + LiAlO_2 \tag{10}$$

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In general, if the reaction products contain (OH) groups with no free water, H_2 is produced stoichiometrically from H_2O, i.e., in a 1:1 ratio. If free water is present in the reaction product, the ratio will be less than 1, as in Reaction 1. If oxides are contained in the final product, the ratio will rise, becoming eventually 2, as in Reactions 9 and 10. The controlling factor in each case is reaction temperature, and the possibilities of intimate mixing, which are governed by melting point and convection considerations. In the application envisaged, the only available water for reaction is the product from the proton-exchange-membrane fuel cell (PEMFC), in which one H_2O molecule is produced for each H_2 molecule consumed. Hence, as a minimum, the reaction products should be those in Reactions 2-4 and 7, 8, so that hydrogen production is stoichiometric.

Theoretical specific Ah capacities of some hydrides are given in Table 1 (as Ah/g and Ah/l), and Table 2 indicates the weights of hydride which will provide 100 W (average) at three PEMFC cell voltages, assuming a stoichiometric (i.e., unit) H_2/H_2O ratio.

Table 1. Calculated Capacities of Hydride Materials

Hydride	Theoretical Density (g/cm^3)	Ah/g	Ah/ml
LiH	0.78-0.81*	6.74	5.26
CaH$_2$	1.90	2.55	4.85
LiAlH$_4$	0.92	5.65	5.20
LiBH$_4$	0.66	9.83	6.49
NaBH$_4$	1.07	5.56	5.17
KBH$_4$	1.18	3.97	3.36

* Depending on source

Table 2. Mass of Hydride (100% Utilization) to Provide 100 W (Mean) for 180 Days as a Function of Fuel Cell Operating Voltage (Specific Energies, kWh/kg, in Parentheses).

Cell Voltage (V)	LiH, kg (kWh/kg)	LiBH$_4$, kg (kWh/kg)	LiAlH$_4$, kg (kWh/kg)	CaH$_2$, kg (kWh/kg)
0.80	80 (5.4)	55 (7.8)	96 (4.5)	212 (2.0)
0.75	85 (5.1)	59 (7.3)	102 (4.2)	226 (1.9)
0.70	91 (4.7)	63 (6.8)	109 (4.0)	242 (1.8)

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3.2.2. Subtask 1.2.2. Reactor Design

A hydrogen generator intended to operate as part of a closed-circuit system consuming hydrogen and producing an equivalent amount of product water, which in turn reacts with the hydride to produce a continuing supply of hydrogen, is not a simple system to design. If the system is to be autonomous and require no make-up water, reaction between the hydride and water must take place in a least an exact 1 : 1 ratio. If the reaction has an exact stoichiometry of unity, as is suggested by Reactions 2-4 and 7, 8 above, no hydrogen must be lost from the system, and correspondingly, no product water must be irreversibly lost, e.g., by becoming water of crystallization in the reaction products. Ideally, more hydrogen should be produced than the amount of water consumed to account for any irreversible losses of either species. Alternatively, a sufficient amount of water must be initially provided to overcome any irreversible losses. For example, if Reaction 1 applies, 80 kg of LiH is required for 18 kW-days, but this must be supplemented by 180 kg of water.

The General Electric Company developed a 1.8 kWh self-contained fuel cell system using a generator of Kipp type as early as 1967 (Table 3). A U.S. Patent was filed in June 1972, which was issued in June 1974 [1]. This operated on $NaAlH_4$ and $NaOH$ as reactants, which allowed it to be used at low ambient temperatures. The reactor is shown schematically in Figure 2.

Table 3. Design Characteristics, General Electric 1.8 kWh Self-Contained Fuel Cell Power Supply

Total Weight:	10.1 kg
Total Energy Stored:	1844 Wh
Energy Density:	170 Wh/kg
Dimensions:	17 cm OD x 20 cm heigth
Continuous Power:	0.45 W
Pulse Power:	7.9 W

More recently, AF Sammer Corporation (J. Blanford Jr., and O. Adlhart) has developed a small, load-responsive hydrogen generator whose output is controlled by the rate of water supply [2]. The generator contained 128 g of LiH (i.e., 863 Ah theoretical), and it would permit a generator energy density (without the fuel cell and control system) equal to 3 kWh/liter at a fuel cell voltage of 0.85 V. A 50 kWh generator is being developed for unmanned underwater vehicles. These generators use a stainless steel cylindrical reactor operating at 50 psig, and incorporating hydride cartridges (either CaH_2 or LiH). The interior of the cartridges are spirally-wound, and the whole cartridge consists of stainless steel perforated sheet-metal. The top of the reactor is fitted with cooling fins, so that hot pressurized water drips back onto a horizontal wick, which is preferentially placed at the bottom of the container. Pressurized hydrogen exits from the top. The concept is shown schematically in Figure 3. The hydrides may have coatings or additives, such as waxes or rubber materials, to give a controlled reaction rate [3].
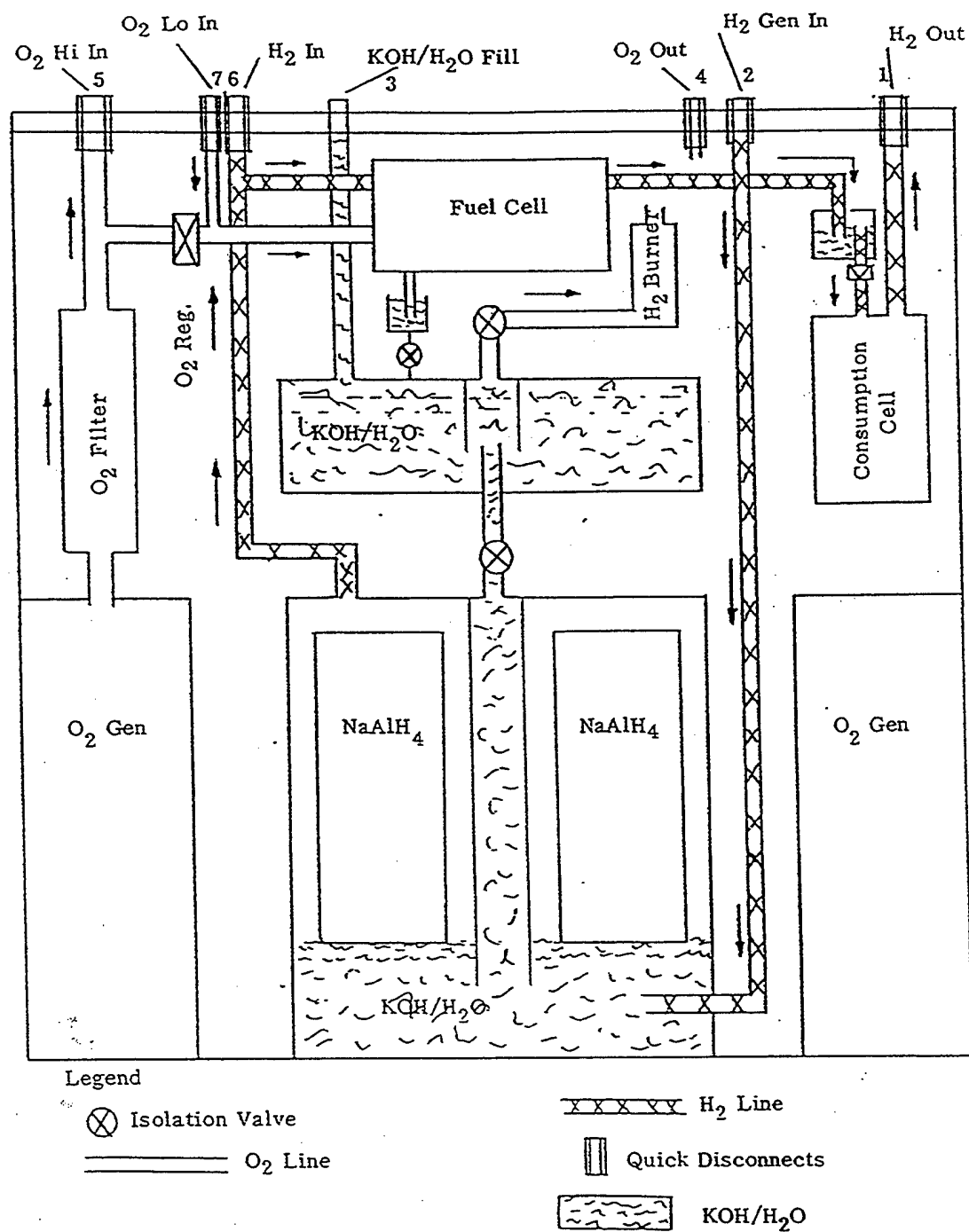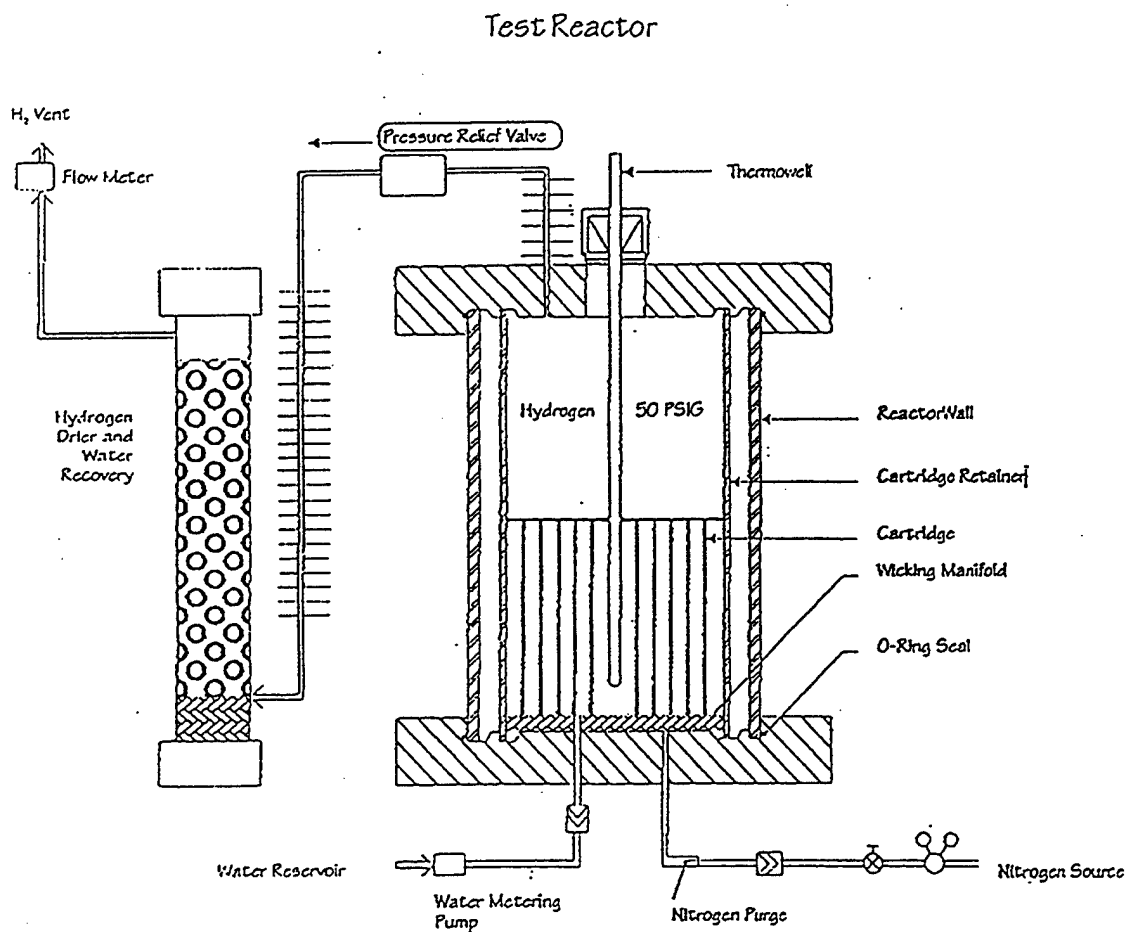
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Figure 2. General Electric Company Kipp Hydride Generator [1].

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Test Reactor

AF SAMMER CORP.

Figure 3. AF Sammer Corporation Conceptual Pressurized (50 psig) Hydride Hydrogen Generator.

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3.3. Task 1.3. Selection and Evaluation of Lightweight Hydrides

3.3.1. Subtask 1.3.1. Design and Construction of Test Cell

The first hydrogen generator constructed and tested was one of Kipp type, which was used for the preliminary measurement of reaction rates for as-received and coated hydrides. The design is shown schematically in Figure 4.
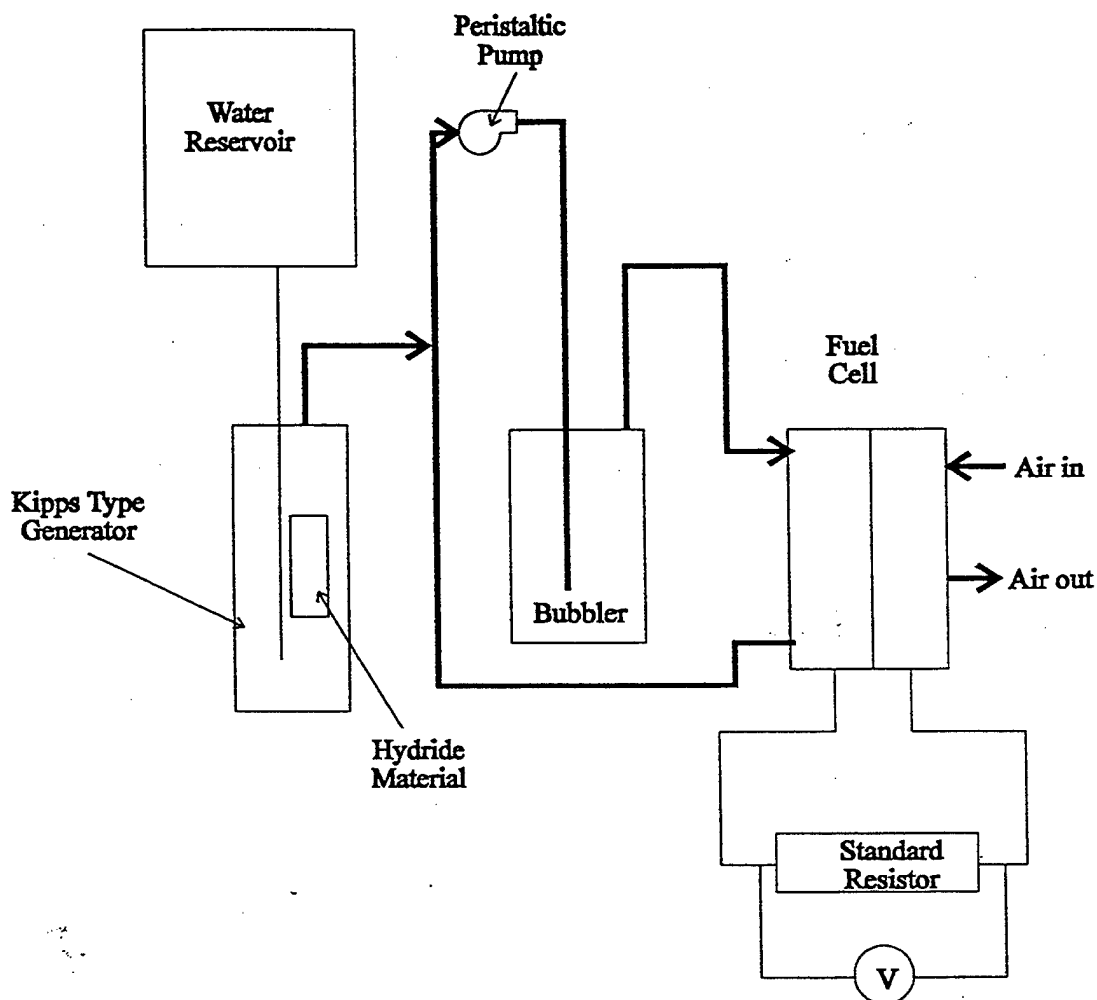

Figure 4. Schematic of Initial Experimental Hydrogen-Generator Fuel Cell System.

The hydride was contained in a nickel-mesh pocket and reacted with water. The rate of the reaction changed as a function of hydrogen pressure, i.e., rate of hydrogen consumption. A peristaltic pump was used to circulate hydrogen through a bubbler for humidification and thence to the PEMFC. After calibration, it also served to measure the volume of hydrogen produced, which could be compared with the rate of hydrogen consumption, i.e., the integral of fuel cell current as a function of time. A second generator was built to determine the quantity of water required for completion of the hydrogen formation reaction. It consisted of a stainless steel cylinder fitted with gas outlet ports, which was loaded with a given hydride under inert

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atmosphere. Controlled amounts of water were added, governing the overall reaction rate, and the quantity of hydrogen released was measured volumetrically (Figure 5).
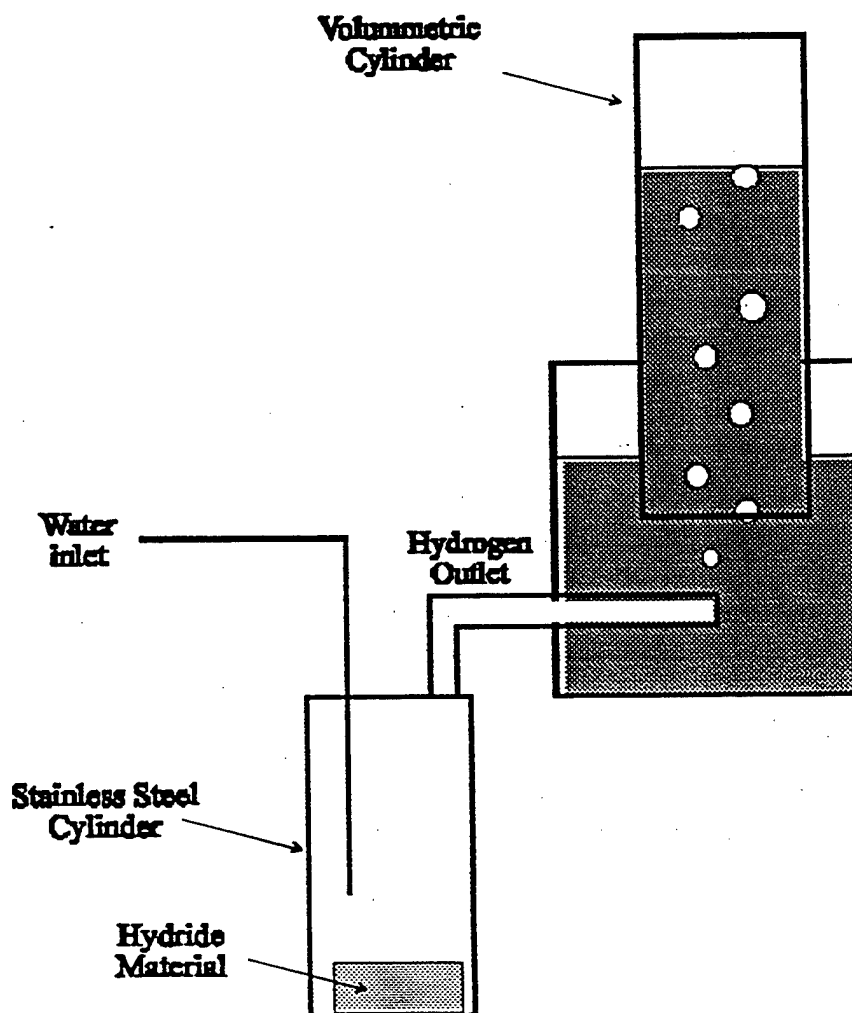
Figure 5. Water-Controlled Chemical Hydride Reactor (Schematic).

3.3.2. Subtask 1.3.2. Experimental Evaluation of "As-Received" Materials

"As-Received" hydride materials initially examined for rate of hydrogen release and conversion efficiency included LiH (with coarse particle size and finely ground), LiBH$_4$, an LiH/LiBH$_4$ mixture, and CaH$_2$. The corresponding theoretical reactions were (1), (3), (1 plus 3), and (8). In each case, a small quantity of each hydride was weighed, and the equivalent amount of water added. The quantity of hydrogen released was measured volumetrically. The yields (theoretical volume of hydrogen at NTP in parentheses) were:

(1) Coarse LiH (0.221 g, 0.501 g H$_2$O; 623 ml): 200 ml (32.1%) initially produced; 630 ml (100%) produced after adding excess water.

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(2) Fine LiH (0.244g, 0.553 g H_2O; 688 ml): 413 ml produced without excess water (60.0%).

(3) LiBH$_4$ (0.12 g, 0.197 g H_2O; 494.3 ml): Very low initial reaction rate. 100% conversion on addition of excess H_2SO_4.

(4) LiH (0.148 g, 0.336 g H_2O; 417 ml) plus LiBH$_4$ (0.065 g, 0.215 g H_2O; 267 ml): Very low initial reaction rate. H_2 released only after direct injection of H_2O into reactor. Reaction probably pH dependent, since final pH was 11.9.

(5) CaH$_2$ (0.82 g, 0.703 g H_2O; 876 ml). 650 ml (74.5%) released with 1.5 hours, 830 ml (94.7%) over 15 hours.

Following these preliminary tests, experiments with as-received materials were conducted at elevated temperature. While LiH does not decompose when heated, the hydroxide monohydrate LiOH.H_2O decomposes at 125 °C, releasing its water molecule. By carrying out the reaction at temperatures above 125 °C, it was shown that it was possible to produce a stoichiometric amount of hydrogen. LiBH$_4$ is also thermally stable, and when reacted with water above 100 °C it produces hydrogen at a steady rate, corresponding to the stoichiometric amount.

It is therefore shown to be advantageous to design a reactor to operate at elevated temperature, which in principle could use the product water from the PEMFC for hydrogen production in the correct stoichiometric amounts.

It was decided not to perform experiments with encapsulated hydrides, because it was considered advantageous to control the hydrogen production rate in the proposed reactor to correspond to the rate of delivery of hydride material into the reaction zone, rather than to control the rate of water delivery, as in as Kipp generator. This was because a reactor operating at temperatures in excess of 100°C requires a steam input, unless the reactor is pressurized.

3.4. Task 1.4. Modeling Studies

3.4.1. Subtask 1.4.1. Preliminary Studies

To accomplish the project goals, a proton exchange membrane fuel cell (PEMFC) stack must be integrated with the hydrogen generator. The efficiency of the stack and the amount of heat generated must be taken into account in the final design. Figure 6 is a schematic of the complete hydrogen generator and fuel cell stack. In this design concept, the hydrogen produced would be circulated in a closed loop, to ensure 100% utilization and to fully use the water produced on the anode side of the PEMFC stack. The exhaust air would be cooled, and the condensed water fed to the hydrogen generator. Table 4 lists the design characteristics of the PEMFC stack. The assumed stack efficiency is 60% during high power load periods and close to 73% during standby periods.

These design characteristics indicate that the required amount of low-equivalent-weight reactive hydride (as LiH at 100% utilization) during peak power generation, assuming 100% fuel cell hydrogen utilization, will be 41 mg-A^{-1}s^{-1} of LiH per unit cell. This amounts to a total

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rate of hydride consumption of 12.3 mg-s^{-1} of LiH, with a corresponding rate of water consumption of 32 mg-s^{-1}. The heat generated from the LiH reaction will be 157 W during periods of peak power.
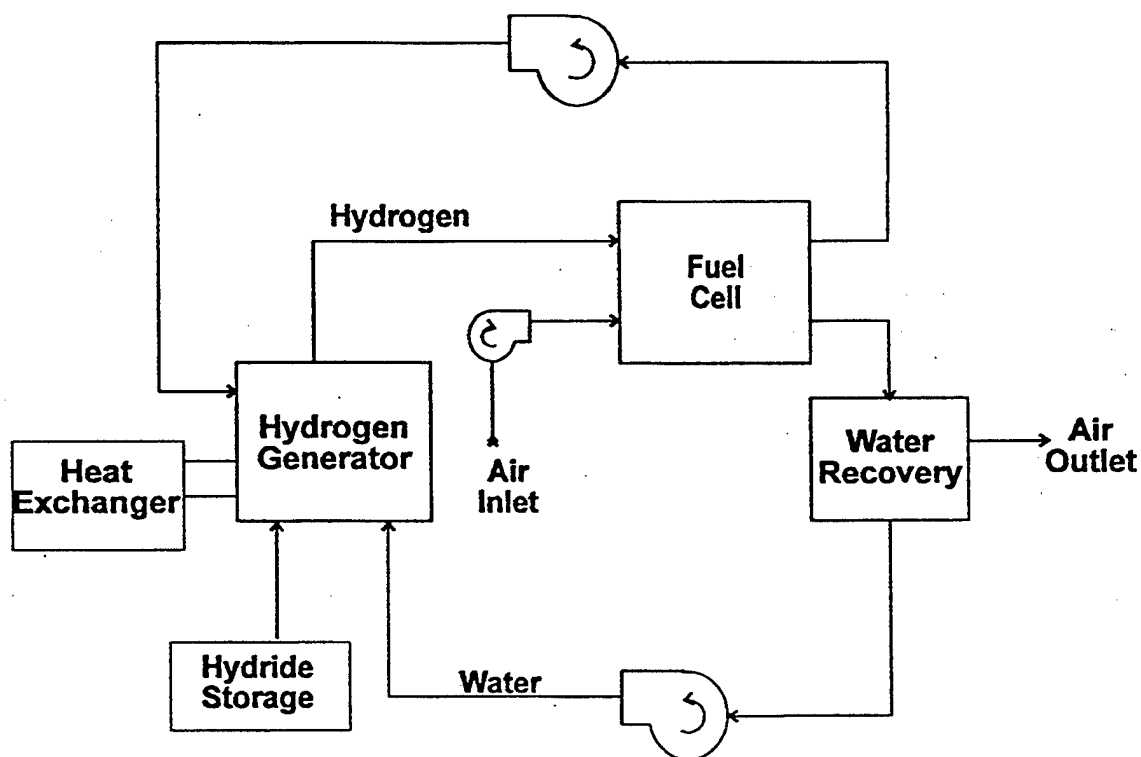
Figure 6. Schematic of Combined Chemical Hydrogen Generator/PEMFC Stack.

Table 4. Design Characteristics of PEMFC Stack

Cell Voltage:	0.75 V
Current Density:	0.200 A/cm^2
Active Area:	100 cm^2
Number of Cells:	15
Total Current:	20 A
Stack Voltage:	12.75 V
Temperature:	70 °C
Electric Power:	300 W
Heat Generated:	117 W
Duty Cycle:	20 min. 300 W; 40 min. 10 W
Stack Dimensions:	15 x 15 x 15 cm

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The technological challenges which must be addressed during the development phase are:

- Controlled rate of H_2 generation for a 6 months period,
- Automated control for pulse power requirement,
- Thermal management,
- Water management,
- As close to 100% reactant utilization as possible, and
- Reliability and safety.

3.4.2. Subtask 1.4.2. Modeling Design of a 5 W Reactor

Based on the experimental data on hydrogen production at elevated temperatures, it was decided to design a chemical hydrogen generator operating under these conditions which would produce sufficient hydrogen for continuous operation of an integrated 5 W PEMFC stack. Preliminary calculations for the size of the reactor were performed. Figure 7 is a schematic representation of the moving-bed hydrogen production reactor.
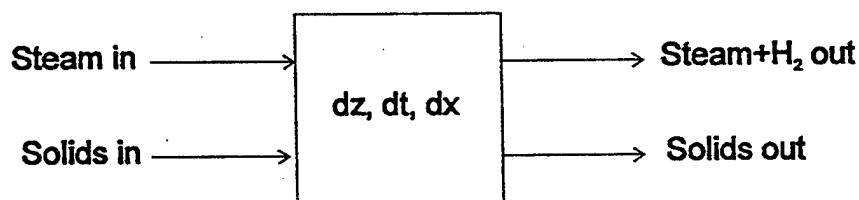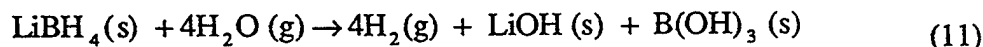

Figure 7 Schematic Representation of Moving-Bed Hydrogen Generation Reactor

A model of the reactor will be illustrated by the use of LiBH4 as the reactant. For a reactor containing LiBH4, the hydrogen generating reaction, assuming H2O to be in the vapor phase, may be represented as follows:

$$LiBH_4(s) + 4H_2O(g) \rightarrow 4H_2(g) + LiOH(s) + B(OH)_3(s) \qquad (11)$$

It seems most probable that the diffusion of water vapor to reaction sites will be the rate limiting process, thus, a "shrinking-core" model may be used to calculate the rate of the reaction as a function of time and of position in the reactor. Figure 8 schematically represents the shrinking-core model. In this model, the reaction proceeds at the surface of a sphere of radius r. Water vapor diffuses through the solid hydrates reaction product layer to the shrinking unreacted core, where it produces more solid hydrates and gaseous hydrogen, which diffuses back to the gas phase. Simplifying assumptions for the model are:

- Simple shrinking-core with uniform product thickness
- Plug-flow reactor
- Uniform spherical particles
- Reaction enthalpy change independent of fractional conversion
- Reaction limited by diffusion of water vapor reactant, not hydrogen product, and
- Isothermal system (i.e., constant temperature coolant).

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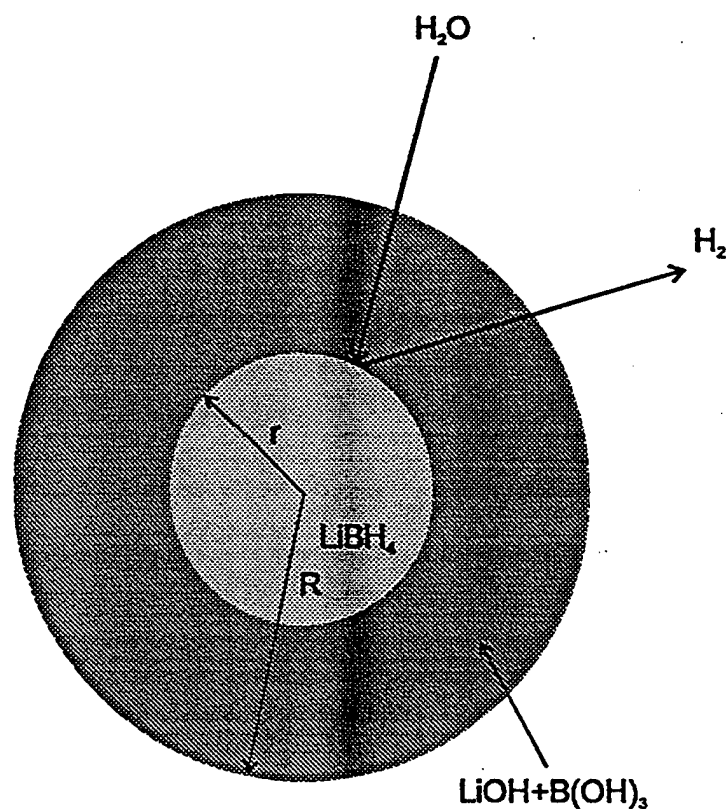
Figure 8 Shrinking-Core model of Solid-Gas Reaction.

A further reasonable assumption is that the diffusion coefficient for water, D_{H_2O} is much lower than that for hydrogen, D_{H_2} i.e.,

$$D_{H_2O} \ll D_{H_2} \tag{12}$$

The extent of conversion, x, can be expressed as a function of the original amount of the reactant. Using the pseudo-steady-state approximation, the rate of increase of x could be expressed by:

$$\frac{dx}{dt} = \frac{\omega^{\bullet}}{3t_o(1-x)[1-(1-x)^{1/3}]} \tag{13}$$

where,

$$t_0 = \frac{R^2}{D_{H_2O}} \quad \text{and} \quad \omega^{\bullet} = \frac{M_A \rho_D}{4M_B \rho_A} \omega_{H_2O,R} \tag{14}$$

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The residence time of a particle in the moving bed reactor can be calculated by integrating Equation (5). Assuming that the mass-flow rate of the solid particles and the volumetric fraction of the solids in the reactor are constant,

$$\frac{G_s}{\rho_s} dt = \varepsilon \, dz \tag{15}$$

$$\varepsilon \approx \frac{\dfrac{G_s}{\rho_s}}{\dfrac{G_s}{\rho_s} + \dfrac{G_g}{\rho_g}} \tag{16}$$

The hydrogen generation rate can be expressed as follows:

$$\frac{dM_{H_2}}{dt} = \frac{4 \, \pi G_{S,in} x_{out}}{M_A} \frac{d^2}{4} \tag{17}$$

for an energy balance:

$$[\text{Accumulation of Energy}] = [\text{Energy In}] - [\text{Energy Out}] + [\text{Energy Exchange}] \tag{18}$$

or:

$$(G_g C_g + G_s C_s) \, dT = \frac{G_s}{M_A} dx \, (-\Delta H) + \pi \, d \, \kappa (T - T_o) \, dz \tag{19}$$

To calculate the conversion of the hydride material as a function of its position in the reactor, Equation (13) can be combined with Equations (15) and (16) to obtain:

$$\frac{dx}{dz} = \frac{\omega^{\cdot}}{3 t_o (1-x)[1-(1-x)^{1/3}]} \frac{\rho_s \rho_g}{G_g \rho_s + G_s \rho_g} \tag{20}$$

The required reactor length, z, for a given conversion, x, can be obtained after integration of Equation (10):

$$z = \frac{12 R^2 M_{H_2O}}{M_{LiBH_4}} \left(\frac{G_g}{\rho_g} + \frac{G_s}{\rho_s}\right) \frac{1}{\omega_{H_2O,R} D_{H_2O}} \left[\frac{1}{14} + \frac{3}{7}(1-x)^{7/3} - \frac{1}{2}(1-x)^2\right] \tag{21}$$

The amount of hydrogen required for a PEMFC output of 5 W, and the corresponding amounts of solids and water vapor is given in Table 5.

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Table 5. Assumed Values of Parameters for 5 Watt Output at 0.7 V PEMFC Voltage and 100% Hydrogen Utilization.

Total Current, A	7.14
Hydrogen generation rate, mole-s^{-1}	3.7×10^{-5}
LiBH$_4$, mole-s^{-1}	9.25×10^{-6}
LiBH$_4$,g-s^{-1}	2.012×10^{-4}
LiBH$_4$, g-s^{-1} at $x = 90\%$	2.24×10^{-4}
G_s, g-cm^{-2}s^{-1}	2.846×10^{-4}
G_{ag}, g-cm^{-2}s^{-1}, stoichiometric	9.42×10^{-4}
G_{ag}, g-cm^{-2}s^{-1}, 2x stoichiometric	1.88×10^{-3}

Figure 9 is an illustration of the functional dependence between reactor length and total conversion, assuming values for certain parameters which are listed in Table 6.
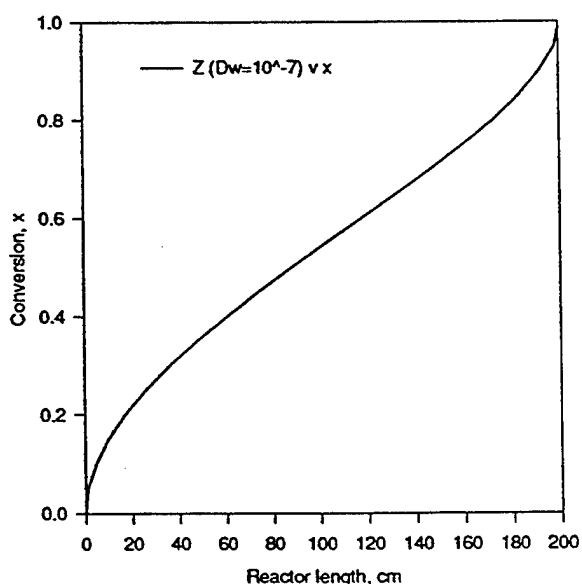

Figure 9. Conversion as a function of reactor length.

The model given above may be extended to the design of an integrated hydrogen generator-PEMFC system. Again, we assume that the reaction is given by Reaction 11. Any new symbols are contained in Table 6. For a PEMFC power output of P Watts, the cell current is given by the following equation:

$$I = \frac{P}{E_{cell}}$$

(22)

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The hydrogen generation rate, n_{H_2}, to sustain this power output at 100 % hydrogen utilization is:

$$n_{H_2} = \frac{I}{2F} \tag{23}$$

The required rate of LiBH4 delivery corresponding to its fractional conversion, x_{out}, at the reactor exit of the reactor is:

$$n_{LiBH4} = \frac{n_{H_2}}{4x_{out}} \tag{24}$$

or:

$$w = \frac{n_{LiBH_4} \times M_{LiBH_4}}{x_{out}} \tag{25}$$

The mass flow rate of LiBH4 per unit cross-sectional area of the reactor is given by:

$$G_s = \frac{w}{\frac{\pi}{4}d^2} \tag{26}$$

From Equations (1) to (5) we obtain:

$$G_s = \frac{M_{LiBH4} P}{2x_{out}\pi d^2 FE_{cell}} \tag{27}$$

The required mass flow rate of water vapor is:

$$G_g = \frac{2sM_{H_2O}P}{x_{out}\pi d^2 FE_{cell}} \tag{28}$$

If there is no pressure drop in the reactor, the linear velocity of the reactant mixture is constant, and the length of the reactor can be calculated as a function of the residence time as follows:

$$L = t_R \frac{G_s}{\rho_s \varepsilon} \tag{29}$$

where ε is given by Equation 16.

Determination of the residence time requires a knowledge of the rate-determining step of the chemical reaction. As above, we assume that diffusion of water vapor to reaction sites is rate limiting, and the shrinking core model may be used to calculate the rate of the reaction as a function of time and position in the reactor, and that the relationship (12) applies for the diffusion coefficients of water vapor and hydrogen through the hydrate product layer surrounding the core. The conversion of hydride reactant, x, can be expressed as a function of the original amount of the reactant, the water vapor diffusion coefficient and several other

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parameters described later. Using the pseudo-steady-state approximation, the rate of increase of x is:

$$\frac{dx}{dt} = \frac{\omega^*}{3t_o(1-x)[1-(1-x)^{1/3}]}$$ (30)

where:

$$t_0 = \frac{R^2}{D_{H_2O}} \quad \text{and} \quad \omega^* = \frac{M_{LiBH4}\rho_b}{4M_B\rho_s}\omega_{H_2O,R}$$ (31)

To achieve a given exit conversion x_{out}, the particle must remain in contact with water vapor for time t_r. The residence time of a particle in the moving bed reactor may be calculated by integrating Equation (30):

$$t_R = \int_0^{x_{out}} \frac{3t_0(1-x)[1-(1-x)^{1/3}]}{\omega^*}dx$$ (32)

To find the dependence of x as a function of position in the reactor, we can substitute Equation (33) into Equation (30):

$$dt = \frac{\varepsilon\rho_s}{G_s}dz$$ (33)

$$\frac{dx}{dz} = \frac{\varepsilon\rho_s}{G_s}\frac{\omega^*}{3t_0(1-x)[1-(1-x)^{1/3}]}$$ (34)

Assuming that the temperature of the cooling fluid is constant and equal to T_0, the energy balance is given by:

$$\frac{\pi}{4}d^2\,(G_gC_g + G_sC_s)\,dT = \frac{\pi}{4}d^2\,G_s dx\,(-\Delta H) - \frac{\pi d}{l}\kappa(T-T_o)\,dz$$ (35)

Combining Equation (33) and (34), and rearranging, we obtain:

$$\frac{dT}{dz} = \frac{G_s(-\Delta H)}{(G_gC_g + G_sC_s)}\frac{dx}{dz} - \frac{4\kappa(T-T_0)}{d\,l(G_gC_g + G_sC_s)}$$ (36)

Equations (35) and (35) may now be solved for the initial boundary conditions:

$$x(0)=0; \quad T(0)=T_0$$ (37)

Table 6. Definition of Parameters and Values Assumed for Moving Bed Reactor Design Calculations.

Symbol	Definition	Unit	Value
M_{H_2O}	Molecular weight of H_2O	g-mole^{-1}	18
M_{LiBH_4}	Molecular weight of $LiBH_4$	g-mole^{-1}	21.75
$\Delta H_{f, LiBH_4}$	Standard enthalpy of formation of $LiBH_4$	kJ-mole^{-1}	−190.5
$\Delta H_{f, H_2O\,g}$	Standard enthalpy of formation of H_2O vap.	kJ-mole^{-1}	−241.84
$\Delta H_{f, LiOH}$	Standard enthalpy of formation of LiOH	kJ-mole^{-1}	−487.2
$\Delta H_{f, H_2BO_3}$	Standard enthalpy of formation of H_3BO_3.	kJ-mole^{-1}	−1088.7
ΔH	Enthalpy change of reaction	kJ-mole^{-1}	−423.7
κ	Thermal conductivity of reactor walls	J-s^{-1}cm$^\circ$C^{-1}	
d	Diameter of reactor	cm	
$z=L$	Reactor length	cm	
l	Reactor wall thickness	cm	
T	Reactor temperature	$^\circ$C	
T_0	Ambient or coolant temperature	$^\circ$C	
G_S	Mass flow rate of solid particles	g-s^{-2}cm^{-2}	
ρ_S	Bulk density of solid particles	g-cm^{-3}	0.66
n_{LiBH_4}	Molar flow rate of $LiBH_4$	mole-s^{-1}	
w	Mass flow rate of $LiBH_4$ powder	g-s^{-1}	
R	Average hydride particle radius	cm	3×10^{-3}
C_S	Heat capacity of solid particles	J-g$^{-1}\,^\circ$C^{-1}	3.5
C_g	Heat capacity of gas phase	J-g$^{-1}\,^\circ$C^{-1}	2.029
ρ_g	Density of saturated steam at 100 $^\circ$C	g-cm^{-3}	5.98x10^{-4}
D_{H_2O}	Diffusion coefficient of H_2O in solid	cm^2-s^{-1}	
ε	Volumetric fraction of solid in reactor		
w_{H_2O}	Mass fraction of H_2O on solid surface		
$t=t_R$	Particle residence time in reactor	s	
x	Conversion		
x_{out}	Final conversion at reactor exit		0.99
n_{H_2}	Molar flow rate of hydrogen	mole-s^{-1}	
G_g	Mass flow rate of gas phase	g-s^{-2}cm^{-2}	
E_{cell}	Average PEMFC cell potential	V	
P	Fuel cell stack power	W	
I	Total current	A	
F	Faraday constant	C-mols^{-1}	
s	Stoichiometric number		96,500

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Equation (34) describes the reactor length, z, as a function of conversion, x. However, several other parameters, e.g., reactor diameter, d, hydride particle size, R, etc., will strongly influence reactor design. Figure 11 shows the reactor length as a function of conversion and of reactor diameter in the form of a three-dimensional diagram. It can be seen that for 1 cm reactor diameter, reactor length has to be at least 10 cm for a conversion of 0.99. Increasing reactor diameter results in a decreased reactant mass flow rate, which may permit a reduction in reactor length. If the reactant particle size is larger, a longer reactor is needed to satisfy the conversion requirements. This is illustrated three-dimensionally in Figure 12.

The correct temperature distribution is an important factor for the safe operation of the equipment. To examine this, the reactor energy balance was numerically calculated to evaluate the temperature variation along the reactor. First, the effect of thermal conductivity of the reactor wall, k, was addressed, as is illustrated in Figure 13. Increasing the thermal conductivity results in a smaller temperature variation along the reactor. The maximum temperature will be lower than 150 °C when the heat transfer coefficient of the reactor wall is k= 0.001 J/s cm °C, which fortunately is the case for most metallic materials. Therefore it should be quite safe to run a stainless steel hydrogen generation reactor under these conditions.
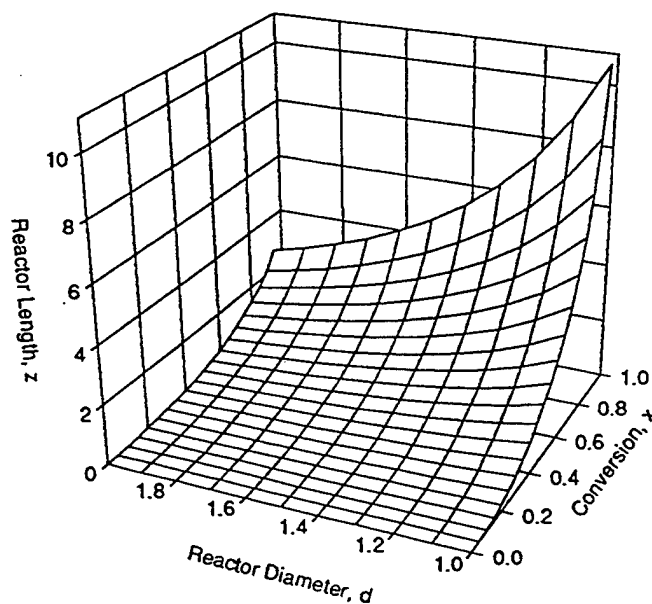

Figure 10   Reactor length as a function of conversion and reactor diameter for 5 Watt hydrogen generator. Other design parameters: Reactant particle radius, R = 0.003 cm; Water vapor diffusion coefficient in solid hydrate, D_{H_2O}, = 10^{-7} cm-s^{-1}; Fuel cell voltage, V = 0.7 V; Stoichiometric number s = 2.
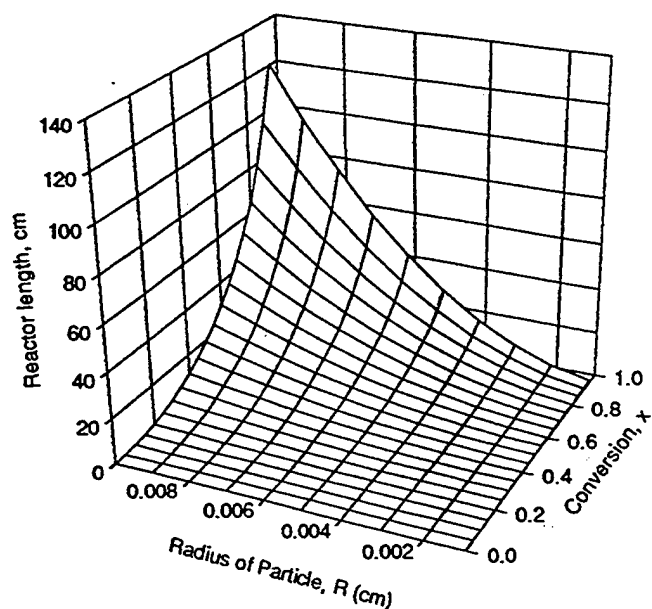
Figure 11 Reactor length as a function of conversion and reactant particle radius for 5 Watt hydrogen generator. Other design parameters: Reactor diameter d = 1 cm. D_{H_2O}, V, and s as in **Figure 10**
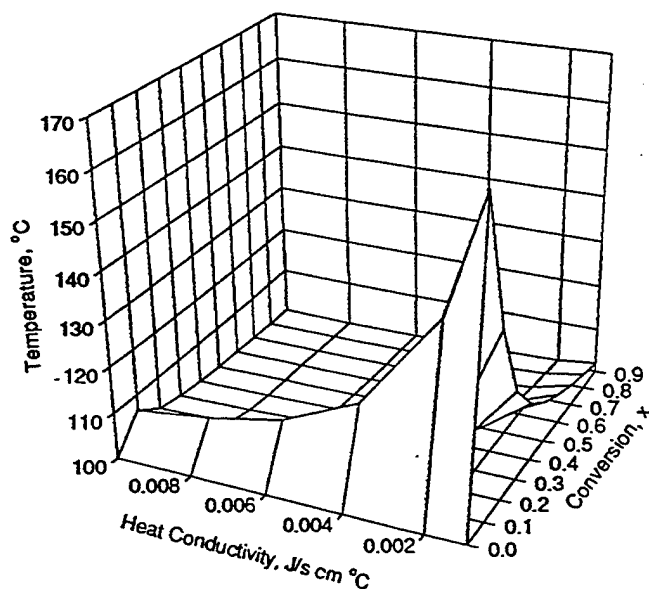

Figure 12. Reactor temperature as a function of conversion and thermal conductivity of reactor wall for 5 Watt hydrogen generator. Other design parameters: R, D_{H_2O}, V, and s as in **Figure 10** and d as in **Figure 11.**

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3.4.3. Subtask 1.4.3. Experimental 5 Watt Reactor

Since the experiments conducted under Subtask 1.3.2 had shown that hydrogen production was stoichiometric at elevated temperatures, a chemical hydrogen generator was designed to produce sufficient hydrogen for the continuous operation of an integrated 5 Watt PEMFC stack. A schematic of the integrated system is shown in Figure 13. The hydride material would be stored in a container and delivered to the reactor via an Archimedean-screw feed system. The steam generator and chemical reactor would be integrated for better utilization of reaction heat and improved heat exchange. A dust collector would retain reacted particles, and the hydrogen evolved would pass through a conditioning condenser. Unreacted hydrogen exiting the fuel cell would be recycled through the reactor. The water produced at the PEMFC anode would be condensed from the exit stream and returned to the steam-generator. Air-cooled heat-exchangers would be incorporated as needed. Initial work involved the construction of the controlled hydride powder delivery system.
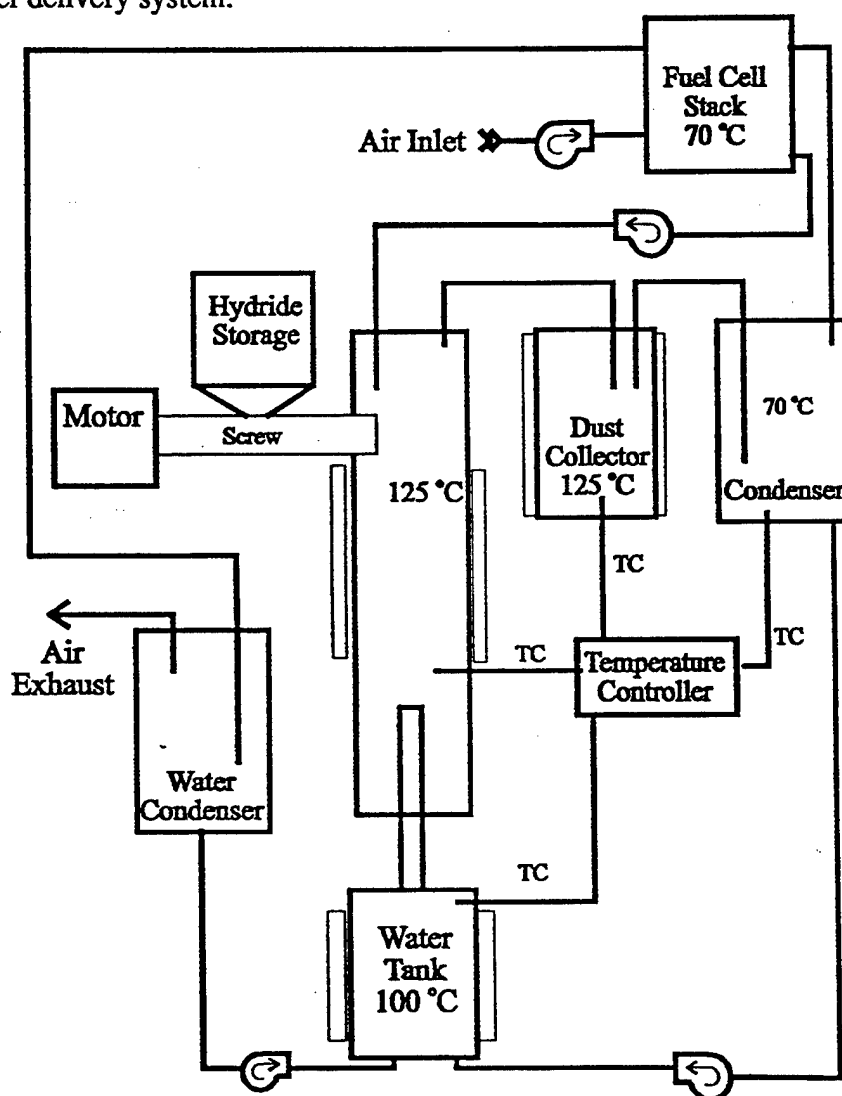

Figure 13 System Schematic, 5 Watt Chemical Hydrogen Generator/PEMFC Stack.

A four cell PEMFC stack capable of delivering 10 W at 0.8 V per cell was assembled and tested. A data-acquisition and control system using an Intel computer with an 8 channel A/D board and two 16 channel expansion boards was designed and built to record system parameters., which include PEMFC and reactor temperatures, gas inlet and outlet temperatures, relative humidities, individual cell voltages and the PEMFC stack current.

By the late summer of 1996, the steam-generator for the 5 Watt reactor had been built and tested with 125°C steam to allow the production of hydrogen at the required rate. The 4-cell PEMFC and the data acquisition and control system were also operational. The key to obtaining a required controlled rate of hydrogen evolution is the hydride powder feed mechanism, which must transport the reactant reliably and at the same time prevent water entering the hydride storage tank. Both screw-type and piston-type powder feed mechanisms were being designed for comparative evaluation.

4. Conclusions

4.1. Choice of Hydride

Of the hydrides examined, lithium had the lowest equivalent weight, and was the most stable. The major problem was the requirement to operate the reactor at a temperature of 125°C if water recovered from the fuel cell exhaust is to be the reactant. Only under these conditions is hydrogen formed stoichiometrically from water molecules. The major design challenges were water recovery, control of reaction rate, and heat removal. A reactor providing 100 W (mean) for 180 days would require 85.1 kg of LiH in a fuel cell operating at 0.75 V. This would consume approximately 192.9 kg of water in a stoichiometric reaction. However, the required hourly duty cycle was a 20 minute period of 100 Wh, followed by a 40 minute period of 6.67 Wh. This longer, low-power period would be at a much lower current density, enabling a higher fuel cell voltage to be used, equal to approximately 0.85 V. Thus, the average requirement is 105.9 W at 0.75 V, corresponding to 90.1 kg (ca. 113 liters solid volume) of LiH and 204.3 kg of water. The 100 Wh/0.333 hours peak requires 1.85 moles of hydrogen, i.e., 60.4 liters of hydrogen at 1 atm pressure and 125°C.

4.2. Generator Design Options

4.2.1. Peaking Generator Operation

There are basically two options for the generation of the hydrogen required for the period of peak power output. The first is to operate the generator at the rate required by the hydrogen demand at any given time. This method of generation is required if the rate of consumption is totally unpredictable, e.g., if the hydrogen is to be consumed in a vehicle with a continuously variable duty cycle. To allow for any inertia between production and consumption, some storage capacity is usually necessary if this option is used. A simple Kipp Generator does not appear to be a viable solution, since the rate of reaction between a reactive hydride (e.g., lithium hydride) occurs too rapidly and generates too much local heating, causing the reaction to be essentially uncontrollable. The heating dries out the material on the surface, but water inside the pores of the material continues to react even after the hydrogen pressure has risen sufficiently to hydraulically push the level of water down below the hydride reactant. After the hydrogen is

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consumed and the water level rises, there is a delay in reaction time to the presence of dried product on the surface, which initially blocks internal porosity. This makes the reactor doubly uncontrollable.

The second option arises when the duty cycle is predictable, which is so in the present case, when the equipment is expected to operate at high continuous power for 40 minutes each hour, then stand by for 40 minutes. The option consists of operating the generator at the mean rate required for the PEMFC, and to store the 60.4 liters of hydrogen produced for the 20 minute peak cycle each hour. Given the volume of LiH reactant required, this should not be difficult, even under ambient pressure conditions. Another option is as a solid hydride operating at 125°C, or at a compromise temperature between that of the reactor and the PEMFC stack. Thus, the best option for this application is a generator which operates at a continuous rate. This greatly simplifies the control system, since a continuous feed of one reactant (the metal hydride) with discontinuous feed of the other (water) can still result in a continuous average production of hydrogen. About 93.7% of the product water is formed at the PEMFC cathode in one-third of the total time the system operates (i.e., during 20 minutes per hour). In other words, provided that the stoichiometric water can be collected and trapped, its supply will not be rate-controlling, and a continuous calibrated screw device may be used to supply LiH at a controlled rate to the reactor. The rate of supply of LiH will be constant, representing the average required load, and it will determine the rate of hydrogen production.

This option is attractive, but it involves three major problems, or rather unknowns, one mechanical, the others chemical. The first is the design of the LiH feed device, which, as we have seen above, must be thoroughly reliable, and must not allow water to pass through to the hydride container. The other two problems are the exact stoichiometry of first, the hydrogen formation reaction, and second, the process for the collection of water from the PEMFC cathode exit. While we have stated above that the stoichiometry of the hydrogen formation reaction goes from 0.5 (product $LiOH.H_2O$) at temperatures <125°C, to 1.0 (product LiOH) at temperatures >125°C, this is an over-simplification. No reaction is exactly stoichiometric. Similarly, the collection efficiency of product water from the fuel cell exit stream can never be 100%. This is illustrated by the mode of operation given below.

4.2.2. PEMFC-Generator Systems

The oxidizing (depleted air) PEMFC exit stream must be separated from the hydrogen anode inlet stream, otherwise hydrogen will be consumed and wasted by reaction with oxygen on the fuel cell anode catalyst. Water must therefore be separated at the highest possible efficiency (as close as possible to 100%) and physically supplied to the LiH reactant in a separate flow-stream. Because water supply is critical in the proposed system, the proposed PEMFC will operate under self-humidified conditions [4, 5] instead of using the usual humidified gas streams, which are saturated to several °C above the stack operating temperature. This procedure requires a total-loss water supply system. For applications where water supply is critical, the PEMFC may be operated so that its temperature is slightly above the dew-point of the gases exiting the cell cathode, containing product water in the form of vapor. Since the minimum oxygen stoichiometry of the inlet air stream giving stable operation is normally 2 (i.e., the highest practical utilization of oxygen in the air stream is 50%), and two molecules of water are formed from every molecule of oxygen consumed, then the exit cathode stream for initially dry air as reactant contains a partial pressure of 0.182 atm. of water vapor, corresponding to a dew point of 58.3°C. This is the maximum marginal temperature of operation of a self-humidified PEMFC, since drying out of the electrolyte membrane, and therefore loss of ionic

conductivity, will take place at higher temperatures. A condenser operating at its maximum possible efficiency at ambient temperature (say 25°C) will still collect only 82.8% of the water vapor exiting a PEMFC operating under self-humidified conditions at 58.3°C, since the saturated water vapor pressure at 25°C is 23.76 Torr (i.e., 0.031 atm).

Clearly a condensing system is inadequate, unless it is associated with a sophisticated vapor recovery system, either using ultra-low temperature condensation or some other method of reduction of the free energy of the system. Instead of trying to produce liquid water more or less inefficiently, then transferring the liquid water to the LiH reactant, use can be made of the very high degree of vapor pressure suppression by chemical reaction of water vapor in the presence of LiH. However, since the cathode exit and anode inlet streams cannot be mixed, means must be found to transfer water in the form of vapor between the two streams.

4.2.3. A Membrane-Humidified System

A possible solution to the above problems is the use of a reactor which uses a Nafion™ membrane (or set of membranes) as a water transporter. This concept relies on the excellent water transport properties and relatively low hydrogen permeability of the Nafion™ membrane, even in ion-exchanged (e.g., Li^+) form. This may allow the product water to be collected from the PEMFC cathode exit stream, so that an equal amount of hydrogen can be produced, provided that the hydride product does not form a hydrate, e.g., $LiOH.H_2O$. This will unfortunately require operation at temperatures exceeding 125°C. Nafion™ is stable enough to operate under such conditions, provided its water transport properties are satisfactory. This may be so if it is in contact with LiOH.

A schematic of the device is shown in Figure 14. We conclude that this may be the only way to make a viable device, but even this may not be reliable. Thus we must concede that the chances of finding a safe, reliable, and chemically secure hydride hydrogen generator are not very great, especially if LiH is to be used, since it will require an operating temperature above 125°C if H_2 is to be produced stoichiometrically from water.

Operation at 125°C, even if successful, will have an operational disadvantage. The system will have some infra-red signature, and if mechanical devices are required (pressure pumps, etc.) reliability and noise may become issues. It should be possible to operate at a lower temperature using an alkaline earth metal hydride, yet still maintain stoichiometric hydrogen production from water. The use of calcium hydride (equivalent weight 21, end product $Ca(OH)_2$) will effectively allow a specific energy of 1.70 kWh/liter, 0.89 kWh/kg in a PEMFC operating at a unit cell voltage of 0.7 V, which is well within specifications. In contrast, LiH (equivalent weight 7.95) offers 1.66 Wh/liter, 2.38 kWh/kg (for LiOH product) under the same cell voltage conditions. Since most systems are volume-limited, rather than mass-limited, for most applications the two hydrides may be practically comparable. Even better is MgH_2, which reacts "violently" with water (so it is unlikely to passivate) and has an equivalent weight of 12.7. It offers 2.90 kWh/liter, 1.48 kWh/kg when used with a PEMFC operating at 0.7 V. Its decomposition temperature of 280°C offers a sufficiently large operating window to ensure that the $H_2O \rightarrow H_2$ reaction goes to completion without side reactions. Beryllium hydride (equivalent weight 5; ca. 7.0 Wh/liter, 3.75 Wh/kg) would be even better, but its decomposition temperature is too low at ca. 125°C, and its products will be highly toxic to many people. An alternative is AlH_3 (equivalent weight corresponding to ca. 3.9 kWh/liter, 1.88 kWh/kg at 0.7 V), but its low decomposition temperature (100+°C) would make its use impractical.
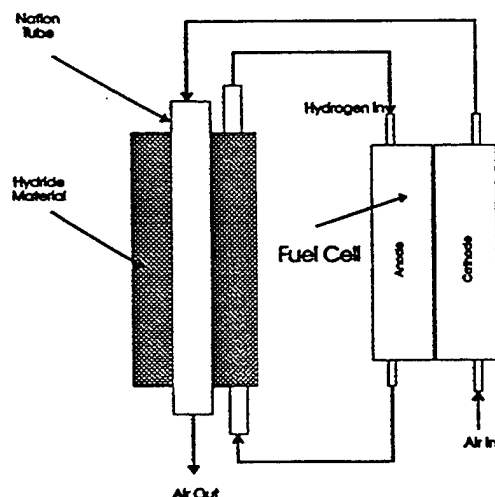
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Figure 14 Schematic Representation of Chemical Hydrogen Generator with Nafion™ Membrane.

4.2.4. Alkaline Fuel Cell Systems

If any alkali metal (i.e., lithium ion) carryover occurs from the reactor via an aerosol in the hydrogen stream to the PEMFC, the latter will be slowly deactivated as ion-exchange takes place. This can be minimized if the Group II systems (CaH_2 and MgH_2) are used. This will be particularly so for Mg^{2+}, which will not form a liquid aerosol with water.

All systems using an acid PEMFC system require a water-exchange device in the form of a condenser or membrane dehumidifier. Such systems cannot be 100% efficient, so in all cases make-up water will be required, and therefore a water management subsystem with active components must be included. This may be complex, and is likely to result in a lack of reliability. We may conclude that a PEMFC system with close to 100% water recovery using CaH_2 or MgH_2 for hydrogen storage in a foolproof system would be a very difficult proposition.

A much more workable solution was given in the original proposal. If the fuel cell is alkaline (with a chemical CO_2 scrubber on the air side), the reactant water is formed in the anode stream, which may be directly circulated over CaH_2 or MgH_2 in a hydrogen feedback loop. This will avoid the problem of product water separation, and permit the program goals to be achieved. It would also be immune from aerosol carry-over of any type. Work on this solution is recommended in future, if the need for this power source still exists.

5. References

1. W. A. Titterington, and R. E. Milgate, General Electric Company, U.S. Patent No. 3,820,956 (June 28, 1974).

2. J. Blanford Jr. and O. Adelhart, AF Sammer Corporation, ."Load Responsive Hydrogen Generator" final report SBIR contract # DAA H01-92-C-R004.

3. G. L. Mackenzie and P. R. Mosher, US Patent 245,676 (December 19 1962)

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4. Texas Engineering Experiment Station; Office of Naval Research Contract No. N00014-95-1-0114, *High Performance Proton Exchange Membrane Fuel Cells: From Electrochemistry and Material Science to Engineering Development of a Multicell Stack* (December 1994-March 1997).

5. Texas Engineering Experiment Station; Department of Energy Contract No. DE-AC08-96NV11985, *Low Cost Lightweight Internal Humidified PEMFCs* (May 1996-June 1997).

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Appendix 2. Energy Storage Efficiency for Direct Methanol Fuel Cells

Direct Methanol Fuel Cell Energy Density

Direct methanol fuel cells (DMFCs) were not considered at this workshop. However, for comparative purposes the energy density for the direct conversion of methanol is presented in this appendix. Research is being conducted on fuel cells which operate on pure methanol vapor feed, and on fuel cells which utilize aqueous methanol solutions. This appendix presents a brief discussion of the energy density for the methanol fuel. The energy densities listed below can be compared with other materials listed in Table 1 of this report.

The table below shows that the theoretical energy density for direct oxidation of pure methanol is 6,200 Whr/kg, which is based on the free energy of the reaction

$$CH_3OH + O_2 = CO_2 + 2H_2O$$
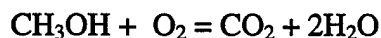
The practical energy density for pure methanol takes into account ohmic and kinetic losses (50% to 75% losses) which are observed in present-generation DMFCs. This does not include the weight of ancillaries.

Another device is the DMFC which uses an aqueous methanol feed. For illustrative purposes, a 1 M solution is typical. If the kinetic and ohmic losses are the same as above, then the practical energy density drops considerably because of the considerable dilution factor (approximately 1 kg of water for 32 g of MeOH).

	Potential Whr/kg	Practical Whr/kg
Pure methanol (vapor feed DMFC)	6,200	1,500-3,100
1 M aqueous solution	198	48-99